

Final Report to RPSEA

REDUCTION OF UNCERTAINTY IN SURFACTANT-FLOODING PILOT DESIGN USING MULTIPLE SINGLE WELL TESTS, FINGERPRINTING AND MODELING

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Executive Summary

Reservoirs containing very high total dissolved solids and high hardness make the field design of a surfactant polymer (SP) flood extremely difficult because surfactant tends to precipitate and separate under these conditions. Under these harsh conditions, elevated levels of various divalent ions, Ca^{2+} , Mg^{2+} , Fe^{2+} in the reservoir brine posed significant challenging issue for designing surfactant formulations for EOR. Over the course of this multiple single-well tests project, different surfactant formulations were successfully developed and tested for multiple field sites based on site-specific reservoir conditions. Performance boosting additives, such as cosurfactants and co-solvents, were also incorporated in the formulations which drastically minimize viscous macroemulsions, promote rapid coalescence under Winsor Type III conditions, and stabilize the chemical solution by reducing precipitation and phase separation. Based on the promising results of batch experiments, the selected surfactant formulations were further evaluated in one-dimensional sand packs and coreflood tests using representative Berea sandstone, reservoir oils, and brines at reservoir temperatures. The procedures used in multiple field single-well tests typically involve injecting 2 to 3 pore volumes of surfactant-only system, without the help of polymer. Results of field tests show the oil recovery ranging from 45 % to 70% of the residual oil (S_{or}) after water flooding. The level of surfactant loading is less than 0.5 wt%. Initial single-well test was completed and successfully verified laboratory results in situ in the presence of high-salinity formation water containing 102,300 mg/L total dissolved solids (TDS). Based on the promising data of initial field test, the validity of this approach (i.e., surfactant-only injection) was further confirmed under even higher salinity (up to 260,000 mg/L) and various reservoir conditions. One pilot interwell-test at a sandstone reservoir was executed in later part of 2013 to further evaluate the effectiveness of surfactant formulation and address technical issues related to scale-up.

The mathematical simulation efforts for this project were executed using multiple approaches to match data from laboratory experiments and field data. From the field production tracer profiles and data, the average S_{or} can be calculated by the retardation of ester over alcohol and given partitioning coefficient. The approximation of S_{or} depends on the validity of several assumptions: 1) Hydrolysis reaction occurs only during shut-in period (no flow), so that tracer B (Material Balance Tracer) and unreacted tracer A (Partitioning Tracer) are exactly together

before back flow begins; 2) S_{or} is uniform throughout the target formation, and 3) The mixing associated with flow through the porous medium affects partitioning and material balance tracers in the same way.

A Single Well Chemical Tracer Test (SWCTT) was used to monitor results of single-well oil mobilization tests. Due to the complex field test processes and geological uncertainties, popular reservoir simulator CMG STARS was selected to model the SWCTT because of its good computational capabilities and chemical reaction features. Permeability, porosity, payzone thickness and partitioning coefficient were treated as input data. Partitioning coefficient of the tracer(s) was measured in the lab under reservoir temperature and formation water salinity. The number of layers, S_{or} , dispersivity coefficient, flow fraction in each layer, and reaction rate were used as the matching parameters. Results of three representative SWCTT tests were numerically interpreted. In dealing with the tracer material balance from field test results, the concentrations of the selected partition tracer (ethyl formate), conservative tracers (methanol and n-propanol) were kept constant and the flow rates of primary tracer and pusher injection were adjusted by multiplying the percentage of recovery to streamline the prediction procedures.

In this endeavor, we also developed and completed a geochemical study of crude oil-composition analyses, including 1) crude SARA fraction analysis, 2) oil fingerprints analysis. In addition, we also completed a petrophysical study of reservoir sandstones using tool such as the Nuclear Magnetic Resonance spectroscopy (NMR) method to investigate Berea sandstone.

Our results show that surfactant-only chemical EOR (cEOR) is a promising technology for existing waterfloods and would provide a competitive alternative to horizontal drilling and hydraulic fracturing. We have also accumulated convincing evidence that good performance in sand packs is predictive of performance in core floods and in single-well tests for surfactant-only cEOR. Our economic analysis of the surfactant-only flooding leads to the conclusion that it has great economic viability than surfactant-polymer flooding or alkaline surfactant-polymer flooding, and that the only remaining technological barrier is reduction of surfactant adsorption. We believe this issue is best addressed with sacrificial agents and/or the use of surfactant carriers.

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Project Fact Sheet

Project Name : Reduction of Uncertainty in Surfactant-Flooding Pilot Design using Multiple Single Well Tests, Fingerprinting, and Modeling

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Objectives: The aim of the project is to use single well test as a design tool to streamline site-specific field data collection tasks to reduce markedly the uncertainty of surfactant flooding pilot design.

Approach: By conducting multiple single-well Surfactant-Polymer (SP) flooding tests, crude oil fingerprinting, and modeling of the single well tests, we can reduce the uncertainty in the SP pilot. The project also targets SP formulations for high TDS brines to reduce the need for surface facilities associated with water treatment. The extent of oil mobilization during the single well tests will be verified by comparing pre- and post partitioning tracer tests. Multi-scale models of the SP single well tests will be used to refine the pilot-scale simulation.

Accomplishments:

1. Several potential binary and ternary surfactant-only formulations are successfully developed for high salinity formations in this study based on batch and sand pack column experiments,
2. For tight formations, injection of polymer created some technical challenges to achieve high oil recovery (< 40% oil recovered in the column), thus we successfully removed polymer (s) from the surfactant formulations and were still able to obtain high recovery,
3. The newly developed surfactant-only system and formulations (between 0.5 to 0.75 total wt%) were tested in multiple single-well locations and an interwell pilot test to verify their

performance,

4. Pre- and post-chemical flood tracer tests were used to assess the residual saturation and the performance of oil recovery by surfactant injection,

5. We developed numerical simulation approaches and completed the effort in numerical interpretation for multiple sites and tracer tests,

- a. Single Well Chemical Tracer Test (SWCTT) – 5 sites,
- b. Interwell tracer test (IWTT) – 1 site,
- c. Simulation of laboratory sand pack tests and core flood experiments – a variety to mimic a range of reservoir conditions

6. Developed and completed geochemical study of crude oil-composition analyses, including

- a. crude SARA fraction analysis,
- b. fingerprints analysis,

7. Completed petrophysical study of reservoir sandstones using tools such as Nuclear Magnetic Resonance spectroscopy (NMR) to investigate Berea sandstone.

8. On the technology transfer, we have made multiple RPSEA workshop presentations (e.g., KS, TX, CA, IN). In addition, we presented technical papers at national conferences (ACS, SPE). We also published several paper abstracts to national conferences (AOCS, AIChE). We are also currently completing multiple papers for the refereed literature and one patent disclosure. The accomplished of the documentation effort is summarized below,

1. Budhathoki, M., Hsu, T.P., Lohateeraparp, P., Roberts, B.L., Shiau, B.J., and Jeffrey H. Harwell, J.H., “Designing of Optimal Middle Phase Microemulsion for Ultra High Saline Brine using Hydrophilic Lipophilic Deviation (HLD) Concept, Colloids and Surfaces A: Physicochemical and Engineering Aspects, in submission (2015).

2. Harwell, J.H., Hsu, T.P., Roberts, B.L., Shiau, B.J., Budhathoki, M., Lohateeraparp, “Binary and Ternary Surfactant Blends for Enhanced Oil Recovery in Reservoir Brines with Extremely High Total Dissolved Solids, U.S. Patent Application No. 14/546,972 (2014).

3. Hsu, T.P., Lohateeraparp, P., Roberts, B.L., Wan, W., Lin, Z., Wang, X., Budhathoki, M., Shiau, B. J., and Harwell, J. H. “Improved Oil Recovery by Chemical Flood from High Salinity Reservoirs-Single-Well Surfactant Injection Test” Paper SPE 154383, presented at the EOR Conference at Oil and Gas West Asia, Muscat, Oman, 16-18 April, 2012.

4. Jin, L.C., Jamili, A., Li, Z.T., Lu, J., Luo, H.S., Shiau, B.J., Delshad, M., Harwell, J.H., “Physics based HLD-NAC Phase Behavior Model for Surfactant/Crude Oil/Brine Systems,” Journal of Petroleum Science and Engineering, in submission (2015).

5. Shiau, B.J., Hsu, T.P., Lohateeraparp, P., Wan, W., Lin, Z.X., Roberts, B.L., Harwell,

J.H., 2012. "Improved Oil Recovery by Chemical Flood from High Salinity Reservoirs," SPE 154260, presented at the SPE Improved Oil Recovery Symposium, Tulsa, Oklahoma, 14–18 April.

6. Wan, W., Harwell, J.H., Shiau, B.J., "Characterization of Crude Oil Equivalent Alkane Carbon Number (EACN) for Surfactant Flooding Design," Journal of Dispersion Science and Technology, (2014).

7. Weston, J.W., Harwell, J.H., Shiau, B.J., Kabir, M., "Disrupting Admicelle Formation and Preventing Surfactant Adsorption on Metal Oxide Surfaces Using Sacrificial Polyelectrolytes [dx.doi.org/10.1021/la501074x](https://doi.org/10.1021/la501074x) | Langmuir 2014, 30, 6384–6388

Significant Findings:

1. Applying theoretical tools like the Hydrophilic-Lipophilic Difference (HLD) equation and concept can significantly reduce surfactant screening time when compared to the conventional method.
2. The developed binary and ternary surfactant-only system can markedly improve recovery of common crude and viscous oil (e.g., 23 cp @ 50 °C) as confirmed in laboratory sand-packed and core flood experiments.
3. Results of multiple field single-well tests indicate significant trapped oil (> 90% reduction of Sor) can be mobilized from the target zone at various reservoir conditions and even tight formation (i.e, permeability of 15 mD).
4. Field pilot multi-wells test (Sept. 2013 – Sept., 2014) indicated that significant surfactant losses (likely due to adsorption) might interfere the field data interpretation and recovery performance.
5. In simulation efforts, due to the complex field test processes and geological uncertainties, numerical simulation method was used to interpret the field test results. Popular reservoir simulator CMG STARS was selected to model the SWCTT because of its good computational capabilities and chemical reaction features
6. Based on the resulting matching profiles of pre-SWCTT and post-SWCTT Sor at multiple reservoirs and locations, we successfully exhibited good surfactant flooding efficiency under various reservoir locations.
7. Based on fingering effort, we observed that crude oil fractions could have impact on the interfacial tensions (IFTs), which is the most critical parameter of EOR.
8. Asphaltenes from different crude oils contain various components, which indicate these crudes may come from different original materials and reservoir conditions.

Future work:

1. Field pilot multi-wells test: additional sites would be selected and screened for potential surfactant flooding. And more pilot tests are anticipated in next twelve to twenty four months (2016-17) based on the encouraging results of multiple single-well

tests and some challenging tasks we met and lessons learned from the first field pilot interwell test.

2. Streamline the design protocols for field scale pilot test based on the conclusions of this RPSEA effort.
3. Development of a single-well surfactant adsorption test. At this point the most important barrier to commercial development of surfactant-only cEOR is the loss of surfactant through adsorption. It is important that a method be developed for verifying the level of surfactant adsorption in the old waterfloods that are the target of this technology.

Chapter 1. Designing Multiple Tracer and Chemical Flooding Tests

1.1 Introduction

Many mature reservoirs with potential for chemical EOR application have high salinities that are problematic and challenging for process design. Because of this challenging characteristic, the alkaline surfactant polymer flood (ASP) becomes economically impossible and technically difficult due to the high cost of water treatment, sludge disposal and the potential scale problem in the formation (Zaitoun et al., 2003). A surfactant polymer flood (SP) would be an option for those reservoirs with very high total dissolved solids (TDS) and hardness in the reservoir brine. However, one of the greatest difficulties in the application of surfactant formulations has been their ineffectiveness in the formation brines having high salinity and divalent ions (Novosad et al., 1982). Injected surfactant must remain chemically stable without exhibiting precipitation and phase separation at reservoir conditions for the duration of the project, which could last for years. If not, the surfactant could be distributed in a non-consistent and unpredictable manner in the reservoir (Puerto et al., 2010). Removing high concentrations of ions by displacement with softer brines is typically not viable due to complicated ion exchange phenomena between reservoir rock and injected fluids, or else unfeasible due to a requirement of fresh water sources. Thus, to overcome the unfavorable high salinity characteristic, it is desired to design a surfactant system which forms a homogeneous, single-phase aqueous solution with formation brines, develops ultralow interfacial tensions (IFTs) with crude oil at reservoir conditions, and has low adsorption on reservoir rocks. Additionally, at high salinities conventional polymers are not effective at increasing viscosity until the polymer concentration reaches economically nonviable levels. These issues favor a consideration of surfactant-only chemical flooding for high salinity and low permeability reservoirs.

It is well known that surfactants with alkoxy chains can provide high salinity and hardness

tolerance. Sulfates and sulfonates having ethylene oxide (EO) and/or propylene oxide (PO) groups have been used in laboratory and pilot tests of surfactant EOR process (Chou and Bae, 1988; Flaaten, 2007; Liu et al., 2008; Levitt et al., 2009; Iglauer et al., 2010; Puerto et al., 2010). Increasing the number of EO groups on the surfactant molecule increases the optimum salinity and tolerance for Ca^{2+} and Mg^{2+} ; PO groups increase the size and area of the surfactant without making it too hydrophilic, which enables lower IFT over a wider range of conditions. However, sulfates are limited to low temperature reservoirs because the hydrolysis of the sulfur-to-oxygen bond takes place above about 60 °C (Talley, 1988). Even though hydrolysis of sulfates can be minimized by adding alcohol to the structure of alkoxy sulfate surfactants during the manufacture (Pope et al., 2010), laboratory screening should be conducted for using sulfates above 60 °C with great carefulness to achieve the required surfactant stability during the entire EOR process. In contrast, sulfonates with alkoxy groups have the required stability at high temperatures because of their sulfur-to carbon bond, which is not subject to hydrolysis. Other sulfonate surfactants without alkoxy groups, such as sulfosuccinic acid ester, are good candidates for creating ultralow IFT with oil and have also been studied and used in enhanced oil recovery and surfactant-enhanced aquifer remediation (SEAR) (Dwarakanath and Pope, 2000; Wu et al., 2002; Rosen et al., 2005; Levitt, 2006; Iglauer et al., 2010; Shiau et al., 2010a., Shiau et al., 2010b).

One of the main criteria for achieving high oil recovery is ultralow IFT between oil and brine. Research has shown that when IFT reached 10^{-2} mN/m and below, residual oil could be mobilized through the injection of surfactant solution (Pithapurwala et al., 1986; Zaitoun et al., 2003; Flaaten, 2007; Levitt et al., 2009; Iglauer et al., 2010; Shiau et al., 2010a). Most coreflood studies indicated that a small slug of surfactant-polymer flood (< 1 PV, surfactant conc. = 0.5-2

%) followed by a polymer drive slug injection could recover 65-97% residual oil saturation (22-47% OOIP). There is a close connection between microemulsion formation and the effectiveness of surfactants in EOR (Shah and Schechter, 1977). The relationship between microemulsion phase behavior and IFT has been well-established, and the ultralow IFT can be achieved by creating middle phase microemulsion (Winsor, 1954; Healy et al., 1976; Huh, 1979; Nelson and Pope, 1978; Pope et al., 1979). The middle phase, which contains equal volumes of water and oil, is observed over a narrow salinity range and can be characterized by an optimal salinity. The maximum oil recovery is expected at the optimal salinity (Healy and Reed, 1974; Healy et al., 1976; Norohna and Shah, 1982). Surfactants with long carbon chain and little branching can form microemulsion and produce lower IFT by closely packing their hydrocarbon tails together. The volume of middle phase microemulsion increases when microemulsion stability rises, which is correlated with a very low oil/microemulsion and microemulsion/water IFT (Bourrel and Schechter, 1988). Highly viscous phases will not easily transport and will perform poorly due to the low pressure gradient in the reservoir which is about 1 psi/ft or less (Levitt et al., 2009). It has been found that a branched hydrocarbon chain is able to decrease the order in the micellar structures, which tends to reduce the microemulsion viscosity, decrease the equilibrium time, and minimize undesirable gel and liquid crystal formations (Levitt et al., 2006). In addition, a more extreme branching with two separate carbon tails stemming from the polar head group has also shown very good performance (Rosen et al., 2005; Levitt, 2006).

Another approach to mitigate the high viscosity problem is adding co-solvents (i.e. alcohols) to surfactant solution. Alcohols, small molecular weight compounds (C4 range), increase the effective surfactant molecular volume at the interface by means of partitioning between the surfactant hydrocarbon groups (Chou and Bae, 1988), to reduce the viscosity of the oil/water

microemulsion (Sanz and Pope, 1995; Levitt et al., 2009). Alcohols, such as pentyl, butyl and propyl alcohols, which have a partition coefficient between the oil and water of nearly one have been used the most in the past few decades. Another advantage of adding alcohols is to increase the surfactant solubility in high salinity brines (Benton and Miller, 1983; Carmona et al., 1985). Carmona et al. (1985) indicated that, at lower temperatures, addition of an alcohol was necessary to prevent sulfonate from precipitating or forming liquid crystals. However, the use of alcohols has been shown to increase the IFT and reduce the oil recovery (Pithapurwala et al., 1986; Smith, 1986). Thus, there are disadvantages and advantages to use co-solvent but the advantages outweigh the disadvantages.

This endeavor describes the development of new surfactant formulations that provide high solubility in high salinities and ultra-low interfacial tensions at low concentrations. The laboratory screening and evaluation of the surfactant, including phase behavior studies, interfacial tensions properties, the surfactant system stability, and the performance of one-dimensional column floods will be briefly discussed. To design a practical EOR surfactant formulation, this research specifically addresses reservoirs with formation brine that has very high total dissolved solids and high hardness, frequently with low permeabilities, and hopes to contribute to future commercial pilot- to full-scale projects in these types of reservoirs. These types of reservoirs have very high residual oil saturations, often greater than 80% of the OOIP. The surfactants studied in this research were obtained from different sources. Table 1 describes the names, origin of the compounds and chemical structures. The primary surfactant used in this experiment was dioctyl sulfosuccinates, or diethylhexyl sulfosuccinates which contains two branched hydrophobic groups in the molecule). Some of other primary surfactants included: Alkyl propoxylate sulfate ($C_{16-17} - 7PO - SO_4^-$), ($C+20$) linear alkyl benzene sulfonate and alkyl

alcohol (C12-C13 100% branched alcohol) propoxylate (with 8 moles of propylene oxide (PO)) sulfate. Co-surfactants used were alkyl ethoxylated alcohol sulfate (sodium laureth sulfate 3 EO), dialkyl (branched C12) sodium diphenyl oxide disulfonate, dialkyl (linear C16) sodium diphenyl oxide disulfonate. Several different short chain alcohols ranging from C3 to C5 were studied for phase behavior experiments which included iso-propyl alcohol (IPA, 70% vol.), sec-butanol (SBA, 99%), diethylene glycol butyl ether (DGBE, 100%) and tert-butanol (TBA, > 99 %). Xanthan gum polymer was used in stability tests, column test and corefloods, but not in the microemulsion phase behavior test. Pure decane (Sigma-Aldrich) was used as representative oil in this study to characterize microemulsion phase behavior and to develop potential surfactant formulations for crude oil. This invention also involved two different crude oils retrieved from the targeted oil fields (reservoir F and reservoir M) managed by Mid-Con Energy (Oklahoma). The viscosities of the crude oil at reservoir temperatures were 7 cp for crude oil F (38° C) and 5 cp for crude oil M (46° C). Surfactant solutions were prepared with both synthetic and reservoir brines. The formation brine from reservoir F (brine F) consists of 46,783 mg/L Na⁺, and 4,400 mg/L Ca²⁺ and 24 mg/L iron, and the total dissolved substance (TDS) is 131,283 mg/L. The site brine from reservoir M (brine M) contains 46,000 mg/L Na⁺, 12,000 mg/L Ca²⁺, 2050 mg/L Mg²⁺ and 150 mg/L iron, and the total dissolved substance (TDS) is 185,000 mg/L.

Part of this RPSEA research efforts from laboratory experiments to field tests involves three aspects of reduction of uncertainty in designing field pilot surfactant-flooding for reservoirs containing very high total dissolved solids and high hardness:

1. Multiple single-well tests targeting high TDS formations (> 10 wt % or 100,000 mg/L):

When reservoir TDS levels reach 100,000 mg/L or higher most currently available surfactant candidates will fall out of the solution because of their solubility limit. Our research in the last few years has focused on developing surfactant formulations that can tolerate up to 300,000 mg/L TDS at low concentrations without the use of cosolvents. We have produced three to five new surfactant formulations suitable for use in high TDS oil fields and verified their performance through several single-well tests conducted in 2011 (Hsu et al., 2012; Shiau et al., 2012).

The advantages of using a single-well test as a design tool include verifying recovery performance of surfactant formulation under actual field conditions, ease of operation, reasonable cost and shorter time-frame for assessment (typically between two- to three-week operations per test). Uncertainty analyses can be conducted for the system design based on multiple single-well data to optimize the performance of a chemical flood. Further economic analyses will also aid in optimization of various parameters (e.g., slug size, and duration) for maximizing the economic return.

2. Advancing surfactant technology and reservoir geochemistry tools for streamlining the design protocols for new surfactant system and selection of potential EOR sites: We will extend recent models relating surfactant structure to optimization of microemulsion formulation through the relationship between the theoretically accessible packing factor (Pf) calculation and the experimentally measurable so-called characteristic curvature (Cc) of the surfactant in the surfactant membrane in a microemulsion. In recent years, we have accomplished this by extending the range of surfactants for which the Cc has been measured to high TDS surfactants applicable for harsh reservoir conditions. In this study, we plan to modify the current Pf calculation procedure to better account for multiple and branched hydrophobes, which we

believe will improve the correlation between the calculated Pf and the measured Cc.

3. Modeling endeavors to account for the site heterogeneity, size of chemical slug, and well placement limitations for chemical EOR design in mature fields: All EOR systems suffer from uncertainties due to the complexity and nature of subsurface geology/hydrogeology. To overcome the potential negative impacts of subsurface heterogeneity a step-up approach will be used in the decision-making protocols. This includes at least discrete steps from bench-scale experiments, core flood, multiple single well tests, pilot field tests, and data evaluation. Our aim is to fill in the gap between the single well tests and the pilot test. The extent of oil mobilization during the single well tests will be verified by comparing pre- and post partitioning tracer tests using reservoir simulation tools. Multi-scale models of the SP single well tests will be used to refine the pilot-scale simulation.

1.2. Single-well Test at H Site

1.2.1. Materials & Methods

There were five chosen single-well and inter-well test sites investigated in this effort. The geologies may vary slightly on their permeability at different locations, mainly are sandstones are located in Oklahoma and Texas. The first site described is at southwestern of Oklahoma near Carter County. The perforated zone of this sandstone formation is between 5994' - 6006'.

Additional site characteristics at the single-well location are listed below,

Permeability Average: 15 mD

Porosity: 15% - 19%

Radius of Investigation: 12-15 ft

Pay Thickness: 9 ft

Temperature of Perf Zone: 123°F

Injection Rate (bbl per day, BPD): 120 (estimated)

Production Rate (BPD): 116

1.2.2. Brine and Oil properties of target site (H site)

Site-specific brine (of H site) was retrieved from the first targeted single-well location and the brine samples were shipped to the lab for analyses of their compositions and properties. The TDS level is determined to be 102,300 mg/L and of which, including individual ions, Na⁺, 21,790 mg/L, Ca⁺², 5855 mg/L, Mg⁺², 1429 mg/L, K⁺, 161 mg/L, Fe⁺², 17.7 mg/L.

Table 1.1. Summary of H site crude oil properties

Oil Properties		Unit
Oil viscosity	25	cp (51 °C)
Oil density	0.896	g/ml
API gravity	26	
Oil EACN	11.3	
Acid number	0.98	mg/KOH g

1.2.3. Surfactants and Polymers

The surfactants studied in this research were obtained from different sources. Table 2 describes the chemical names of the surfactants used. The primary surfactant used in this experiment was dioctyl sulfosuccinates, or diethylhexyl sulfosuccinates which contains two branched

Table 1.2. Surfactant Candidates used for High Salinity Formation

Surfactant	Code Name	Cc
Dialkyl sulfosuccinates	SF01	2.6
Ethoxylated alcohol sulfates	SF02	-2.3
Blends of monoalkyl and dialkyl diphenyloxide disulfonates	SF03	-6.9
Isopropanol	ALC01	n/a

*Cc: characteristic curvature: when value > 0, forming water-in-oil microemulsions, < 0, forming oil-in-water microemulsions

hydrophobic groups in the molecule). Some of other primary surfactants included: alkyl alcohol (C12-C13 100% branched alcohol) propoxylate (with 8 moles of propylene oxide (PO)) sulfate.

Co-surfactants used were alkyl ethoxylated alcohol sulfate (sodium laureth sulfate 3 EO), dialkyl (branched C12) sodium diphenyl oxide disulfonate (Calfax DB-45), dialkyl (linear C16) sodium diphenyl oxide disulfonate. Several different short chain alcohols ranging from C3 to C5 were studied for phase behavior experiments which included iso-propyl alcohol (IPA, 70% vol.), sec-butanol (SBA, 99%), diethylene glycol butyl ether (DGBE, 100%) and tert-butanol (TBA, > 99 %). Two polysaccharide, biopolymers, were selected for a possible surfactant/polymer flood in this effort to minimize the negative impact of high TDS on viscosity reduction and their mobility control performance. The polymers used in this study include Xanthan gum and Scleroglucan. The biopolymers were used in stability tests, column test and corefloods, but not in the microemulsion phase behavior test. Pure decane (Sigma-Aldrich) was used as representative oil in this study to characterize microemulsion phase behavior and to develop potential surfactant formulations for crude oil.

1.2.4. Phase behavior Studies

Dioctyl sulfosuccinates (SF01) and alkyl (C12-C13) branched alcohol propoxylate (8 PO) sulfate (SF05) were first selected to be the primary surfactants in the experiment due to their branched hydrophobe structures. It has been shown that SF01 and SF05 are able to create microemulsion with different hydrocarbon liquids and achieve low IFT with proper cosurfactants addition (Wu et al., 2002; Shiau, 2005; 2006; Hsu, 2006). A 1:1 water/oil ratio was used for the microemulsion test. Prior to crude oil studies, phase behavior studies using decane were conducted with surfactant systems in both synthetic and site brines. With the targeted salinity, the optimal surfactant formulation was obtained by varying the surfactant/cosurfactant ratio in a binary surfactant mixture. The occurrence of middle phase microemulsion was verified by visual observation. Crude oil phase behavior samples were incubated at reservoirs temperatures. Once

the equilibrated condition was achieved, IFT measurement was conducted for the samples. The co-solvent was also added to the binary surfactant system to promote microemulsion formation if necessary. The optimal surfactant formulations from decane studies then were further tested with crude oils. Surfactant/cosurfactant or surfactant/cosurfactant/cosolvent formulations were evaluated using the following typically qualitative criteria:

- Solution stability: aqueous stability of surfactant and surfactant/polymer solutions at reservoir conditions (salinity and temperature) without precipitation and/or phase separation
- Low interfacial tension: IFT is 10^{-2} mN/m or below.
- Coalescence rate: how fast the emulsion brakes after mixing and form a microemulsion in equilibrium with oil and/or brine.
- Undesired phase: ideal microemulsion with low viscosity and, the absence of gelation and liquid crystal formation.

Table 1.3. Surfactants Formulations for H Site Based on Crude oil/Brine Phase Behavior Studies

Surfactant Formulation	Surfactants	Ultralow IFT*
Binary system	SF01/SF02	Yes
Ternary system #1	SF01/SF04/SF02	Yes
Ternary system #2	SF05/SF02/SF03	Yes
Viscoelastic surfactant (VSurf)	SF02 and SF02/VSF02	No
*IFT < 10^{-2} mN/m		

1.2.5. Precipitation and phase separation studies

Various concentrations of surfactant were prepared with either the stimulated or site brine and aged at reservoir temperatures for a minimum of a month and then observed for the appearance of the samples. The presence of precipitate was determined visually based on the fact that surfactant crystals can reflect light. The occurrence of phase separation was also assessed by

visual observation. Phase separation is confirmed to have taken place when two layers form in the solution (Shiau et al., 1995).

1.2.6. Interfacial tension measurements

The interfacial tension between crude oils and surfactant solutions were measured at reservoir temperatures (51° C for H site) using a Grace M6500 spinning drop tensiometer. IFT measurement for decane samples were done at room temperature.

1.2.7. Column tests

Column tests were used to simulate one-dimensional reservoir flow. Figure 1 shows the apparatus for column test in this study. Valuable information can be obtained from column studies including: mobilization enhancement under flow-through conditions, potential pressure drop in the reservoir and unanticipated reactions with reservoir rock. We first crushed the Berea sandstone core and dry packed the column. The porosity of crushed sand was estimated using a 50-mL volumetric cylinder and volume displacement by water based on weight measurement. A vertically oriented jacked Kontes chromatography column (2.5- cm diameter and 15-cm length) was used in this study. A flow-adaptor was also used to adjust the length of the sand pack inside the column. The fluids were delivered through the column from bottom to top. The column was first saturated with formation brine and then a pre-determined oil amount was injected into the column. Continuous brine solution was injected until achieving residual oil saturation (e.g., between 20 to 40% oil saturation). Column effluent samples were collected by a universal fraction collector (LKB Bromma). The temperature of the jacked column was controlled by circulating water from a water bath.

Table 1.4. Initial Results of Total Oil Recovery from Sand-pack Column Studies

Column test #	Injected chemical	Injected slug size	Residual oil recovery
1	Ternary#2/2000 ppm XG polymer	0.5 PV	24%
2	2000 ppm XG polymer	0.5 PV	Plugging
3	Ternary#2/5500 ppm HEC-25 polymer	0.5 PV	23%
4	5500 ppm HEC-25 polymer	0.5 PV	13%
5	1.5% viscoelastic surfactant (Vsurf)	1 PV	0%
6	Pre 1.5% VSurf+ Ternary #2 + Post 1.5% Vsurf	0.1 PV+1.5 PV+0.5 PV	40%

*VSurf: viscoelastic surfactant formulation

1.2.8. Core flood test

The objective of the core flood experiment was to evaluate how effectively a surfactant formulation can recover oil under reservoir conditions. Figure 2 shows equipment setups for core flooding experiment. Mineral oil acted as the displacing fluid, and was driven by a pump to displace the fluids of interest through the core. The one-inch core sample was kept in a convection oven at constant reservoir temperature. Fluid eluting the core was collected into the burette. Berea sandstone with targeted permeability was used for the core flood. The dimension of the core was 1.225-inch long and 1-inch in diameter with a permeability of 20 millidarcy to mimic the targeted site condition. After saturating the core, brine was pump through until the pressure drop was constant. The core was then flooded with 6-PV of oil and subsequently flooded with brine (approximately 6-10 PVs) again to achieve residual oil saturation (about 36%). Then the selected surfactant/polymer and polymer slugs were injected at flow rate of 0.05 mL/min.

1.2.9. Field Tracer Tests at H Site (Pre- and Post-Chemical flood test)

One of the aims for this study is to assess the performance of oil recovery by injecting the developed high salinity surfactant formulations. The partitioning tracer selected is ethyl format based on the reservoir temperature (51 °C) and laboratory treatability study results. Injection of EF and monitoring its breakthrough in the produced fluid allow us to quantify the estimated residual saturation (S_{or}) at the target zone. The concentrations and volumes injected for the

partitioning and conservative tracers are listed in Table 5.

1.2.10. Field Preparation and Testing Procedure

In this study, the chemical tracer injection and chemical flooding were conducted at multiple targeted sites. Though, each individual site (well) has their unique geological and hydrogeological conditions, the general field preparation tasks and testing procedures are briefly discussed below.

Our team would first select the possible well (mostly a producer well) at the targeted site based on their production history and most favorable conditions for the single well test. Once the test well location was decided, the site-specific crude oil and brine samples were collected from the test well and shipped to the laboratory at University of Oklahoma for the surfactant screening tests and determining the partitioning coefficient of the tracer.

Based on the reservoir temperature and the production rate at the test well, we would design the radius of investigation at 10' to 15' for the partitioning tracer and 15' to 20' for the conservative tracer(s).

Prior to the test being conducted, a packer was set one joint above the perforated zone. The packer is intended to isolate the flow of the injected fluids into the perforated interval and prevent entry of injection fluids into the annulus. During the week of the SWTT, we would shut-in the near-by wells to eliminate potential reservoir influences.

Our team would set up a portable field test unit at the field (see Figure 1.6). The field activities schedule was drafted. In general, one to three 500 bbl frac tanks were placed on-site for brine storage and for reuse and re-injection. The rod pump of the test well was unseated first in preparation for the pre-flush to temporarily water out the test zone. The pre-determined volume of brine (between 300 to 700 bbls) was injected during the pre-flush at site-specific average

injection rate on vacuum (between 0.75 to 2 X average production rate). The injected brine was filtered with 1 micron size filter cartridges to prevent plugging of the formation. Injection rate and volumes were recorded during this procedure.

Prior to chemical tracer injection, the rod pump was temporarily resealed and produced back for four to eight hours while recovering the fluid. This crucial step would clean the perforations and helps ensure a good tracer push into the formation. The produced fluids during this period went into one of the frac tanks on-site. The pump was then unsealed for chemical tracer injection and additional fresh water was delivered to the site to provide the required fluids for tracer injection. Once ready, chemical tracer injection was initiated. Initially the injected brine that contained the reactive tracer (EtF), the cover tracer (NPA), and the mass balance tracer (MeOH) was injected. After main tracer slug injection, this was followed by the push slug of brine containing mass balance tracer-only (MeOH). For proper tracer test and chemical flood, the key is to maintain a constant injection rate during these tests (on vacuum). During injection, the tracer solution was sampled and analyzed for tracer concentration by field gas chromatography (GC) (see Figure 1.6).

The well was then shut-in for a pre-determined soak period (between 24 to 72 hours, based on temperature and reaction rate), during which the partitioning tracer (e.g., EtF) hydrolyzed to form ethanol (EtOH), the product tracer. At the conclusion of the soak period, the test well pump was resealed for the pullback production stage. During the pullback, a pre-determined volume (usually between 1 to 1.5 PV) of the fluid were produced over a 24 to 48 hours period. The produced fluid was sampled every 10 to 20 minutes for the first 8 hour and every 30 minutes for the remainder of the test. Samples were analyzed for tracer concentration by GC on site.

Immediately after completion of pre-tracer test, the chemical flooding was initiated to mitigate

any significant change of S_{or} near the test well. The selected surfactant formulation was prepared with the produced brine and the pre-determined PV of surfactant-only solution was delivered into the well with a dedicated pump. Typically after the surfactant injection, a push slug of brine would be injected to move the mobilized oil away from the radius of influence (> 20 ft).

After chemical flooding, the post tracer would be conducted using similar tracers, amount of the required tracer and pusher, and identical procedures as the pre-tracer test. Results of the S_{or} between the pre- and post-tracer test would be used to quantify the performance of the oil removal based on the chemical flood.

1.2.11. Results of Reservoir H Field Test

Our initial observations showed that the ultra-low IFT (0.008 mN/m) has been achieved in our initial efforts using ternary#2 surfactant formulation with site crude and site brine, the resulting column tests did not produce favorable oil recovery level (< 25%). Part of this poor performance is due to the tight formation at the H site (< 100 md). Thus, we made some modifications to explore surfactant-only formulation for tight formation in the further tests.

The second set of column studies indicate the oil recovery increases markedly using one of the modified surfactant systems, including,

1. Propoxylated/ethoxylated alcohol sulfates (SF05): 0.65%
2. Blends of monoalkyl and dialkyl diphenyloxide disulfonates (SF03): 0.05%
3. Ethoxylated alcohol sulfates (SF02): 0.05%

To improve the performance of the surfactant formulation, e.g., increasing the coalescence rate of microemulsion (< 5 mins), and maintaining stable solution over extended period (> weeks), additional formulation modifiers (e.g., chelating agents & hydrophilic linkers, averaging level of

300 to 600 mg/L) were introduced to achieve the performance goal.

1.2.12. Field single-well test design

Figures show the design of the pre- and post-chemical tracer test and surfactant mixing system design. These engineering designs were similar to our previous studies (Hsu et al., 2012; Shiau et al., 2012). The injection of chemicals at the H site was initiated in late April, 2013 and the injection was completed in mid-May of 2013.

Representative photos and the resulted Sor of the field test are shown in Fig. 1.6 and Fig. 1.7, respectively.

Table 1.5. The Designed Tracers, Concentrations and Volume used for the Single-Well Tracers at H Site

(a)

Tracer	Conc., ppm	Volume, BBLs	Total amount to add	
			Gallons	Lbs
EF	10,000	24	12	92.5
1-PrOH	5,000	24	7	46.3
MeOH	3,000	120	21	138.8

(b)

Total Injection Volume, BBL	Volume of EF, BBL	Volume of pusher, BBL	Radius of investigation, ft	
			Partitioning tracer	Nonpartitioning tracer
120	24	96	10.0	13.2

Note: Calculation is based on $K = 3$, $S_{or} = 20\%$ and $\beta = 0.75$

*K: partitioning coefficient for Ethyl Format (EF)

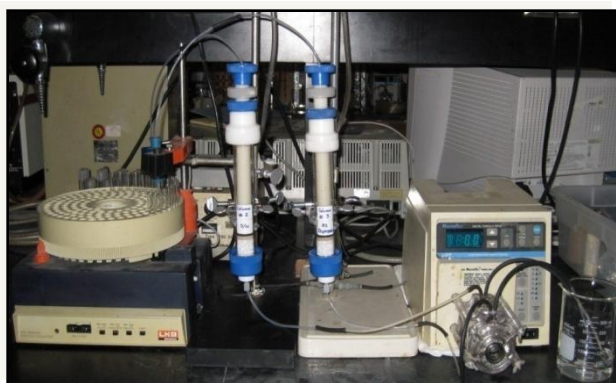


Fig. 1.1—Pump, 2 packed column and sample collector



Fig. 1.2—Core flood apparatus used for the experiments

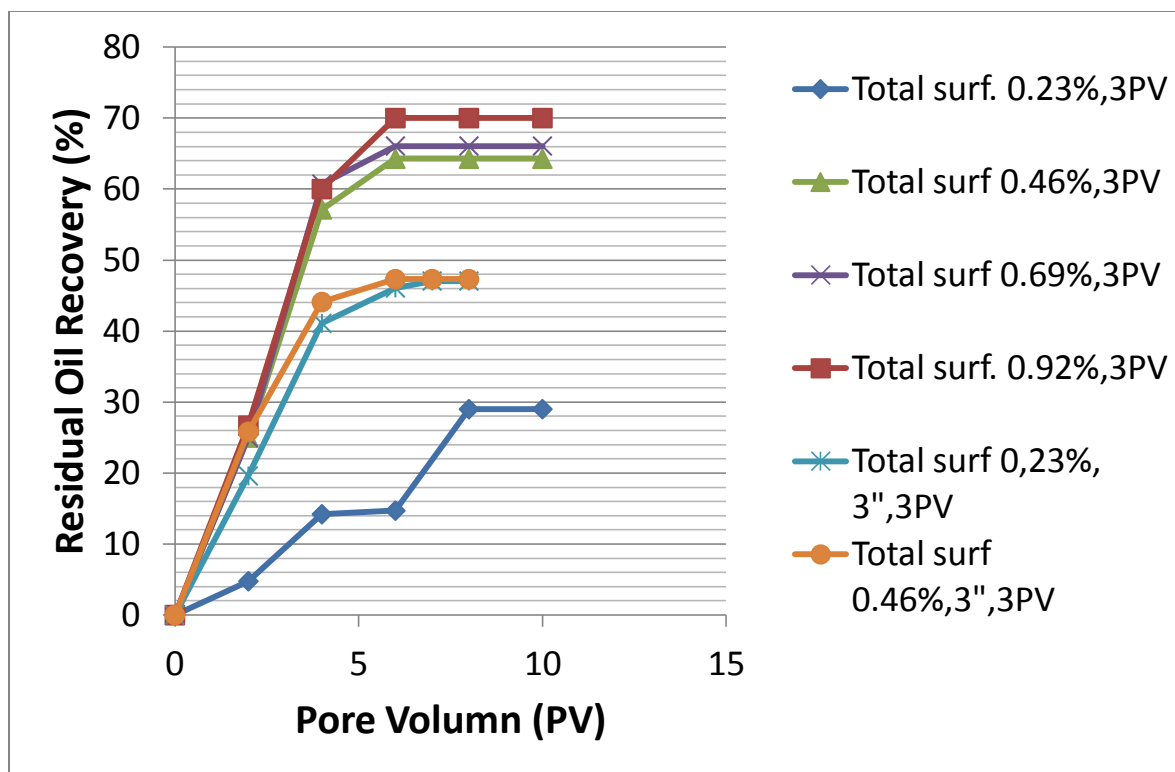


Fig. 1.3—Results of column tests using different surfactant concentrations and the length of the sand-packed column

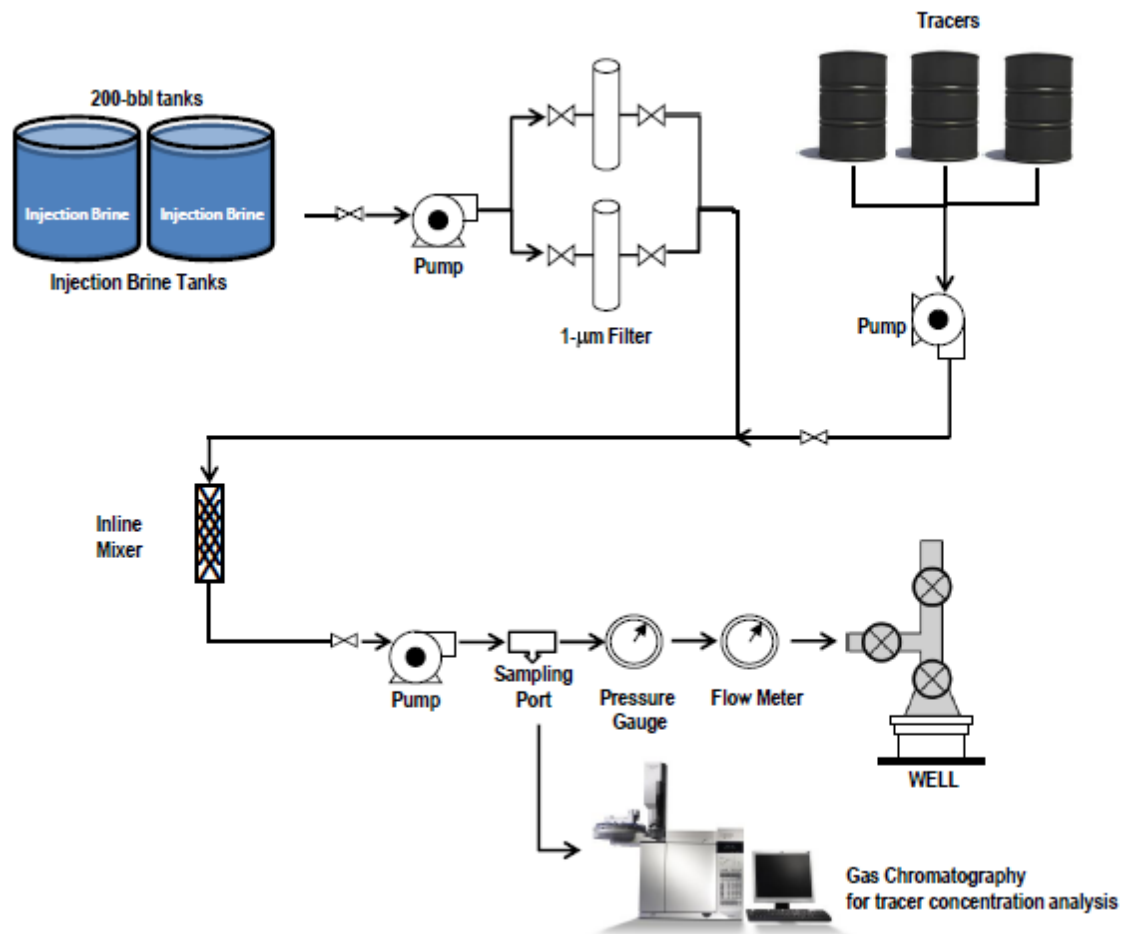


Fig. 1.4—Flow chart of pre- and post-chemical flood tracer tests and their mixing and monitoring design

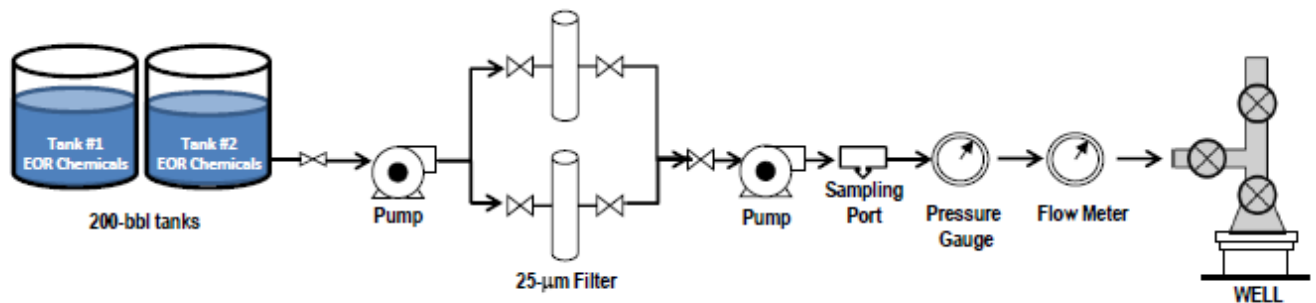


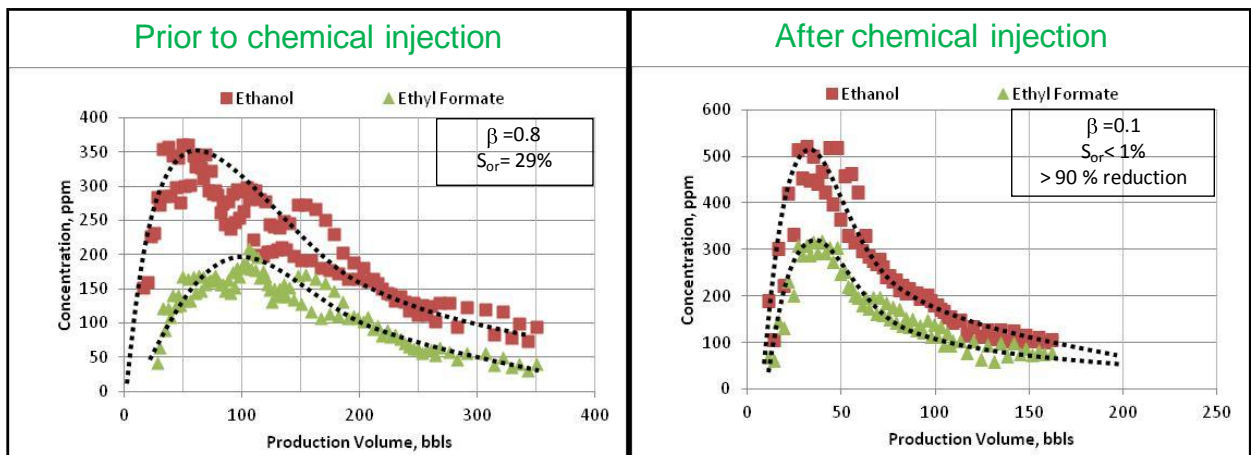
Fig. 1.5—Flow chart of chemical flood injection tests and surfactant mixing design

Single-Well Chemical Test



Fig. 1.6 – Photos of field single-well equipment set-up and lab trailer

Field Results – Pre- and Post-Chemical Flood Tracer Tests



*Beta (β) values: estimated from moment analysis

Fig. 1.7 – Moment analyses of pre- and post-chemical flood tracer tests and the resulting S_{or} and retardation factor, β (H Site)

1.2.13. Summary of the H Site Field Test

Based on the resulting field tests and data comparisons between pre- and post-tracer tests, some important conclusions can be drawn as follows,

- Applying HLD concept can significantly reduce surfactant screening time when compared to the conventional method.
- The TDS of brine can be used as the optimal salinity in HLD equation at high salinity to determine the surfactant selection
- The developed ternary surfactant-only system can markedly improve recovery of viscous oil (23 cp @ 50 °C) as confirmed in sand-packed and core flood experiments.
- Results of field single-well test indicate significant trapped oil (> 90% reduction of S_{or}) can be mobilized from the target zone at a tight formation (i.e, permeability of 15 mD) by surfactant-only flooding
- Field pilot multi-wells test at the H site is anticipated in the near future based on the encouraging results of single-well test, but will be delayed until oil prices stabilize

1.3. Reservoir W Case Study

Reservoir Information. W site located near Guymon, Oklahoma is the oil field for the targeted location where SWCTTs are performed based on its uniqueness of extreme high salinity in the formation. The produced reservoir brine and crude oil samples collected for this site are used for the lab experiments. Table 1.6 shows information on composition of the reservoir brine. Brine analysis is performed by an outside local lab (the Red River laboratory, Oklahoma City).

Table 1.6. Formation Brine Analysis of W Site

Components	Concentration (mg/l)
Sodium	51675
Potassium	1076
Magnesium	2868
Calcium	10105
Iron	10
Sulfate	341
Chlorine	235634
Total hardness (Ca^{2+} and Mg^{2+})	12973
Total dissolved solids	301710

The permeability, porosity, pay thickness, and crude oil viscosity of the W site are reported as 500 to 1000 mD, 15-20 %, 12 ft, and 4.5 cP at the reservoir temperature of 52°C (125 °F) respectively. The wellbore dead volume is 35 bbls and the average equilibrium production rate is 55 bbls/day.

1.3.1. Development of Surfactant Formulations for W Site

Four optimized surfactant formulations have been proposed for this specific reservoir conditions by the hydrophilic lipophilic deviation (HLD) method and is discussed elsewhere (Budhathoki et al., 2015). In this work, the surfactant formulation incorporating $\text{C}_8\text{-(EO)}_1\text{-(PO)}_4\text{-SO}_4\text{Na}$ and SAES is selected as the surfactant flood system for field test because of unavailability of other three extended surfactants in bulk quantity. The extended surfactant, $\text{C}_8\text{-(EO)}_1\text{-(PO)}_4\text{-SO}_4\text{Na}$, used in this study for both lab experiments and field tests is provided by Sasol North America, Inc. SAES surfactant i.e. Sodium laureth sulfate, trade name Steol Cs460, is purchased from Stephan Chemical Inc. F-95 grade Ottawa sand (60-170 mesh size) used in sand packed studies is purchased from U.S. Silica and the tracers: ethylformate (>97%), methanol (>97%), and n-propanol (>97%) used in SWCTT tests are purchased from Univar.

Figure 1.8 shows the IFT measurements of the surfactant system at the various concentrations of SAES. The ratio between $C_8-(EO)_1-(PO)_4-SO_4Na$ and SAES at which the minimal IFT i.e. $8E-3$ mN/m is obtained is defined as the optimal formulation. The aqueous phase of this surfactant system at the optimal condition is reported to exhibit clear homogeneous single-phase solution. Also the coalescence rate is reported to be less than 30 minutes showing that the proposed formulation satisfies the criteria of the cEOR surfactant flood system.

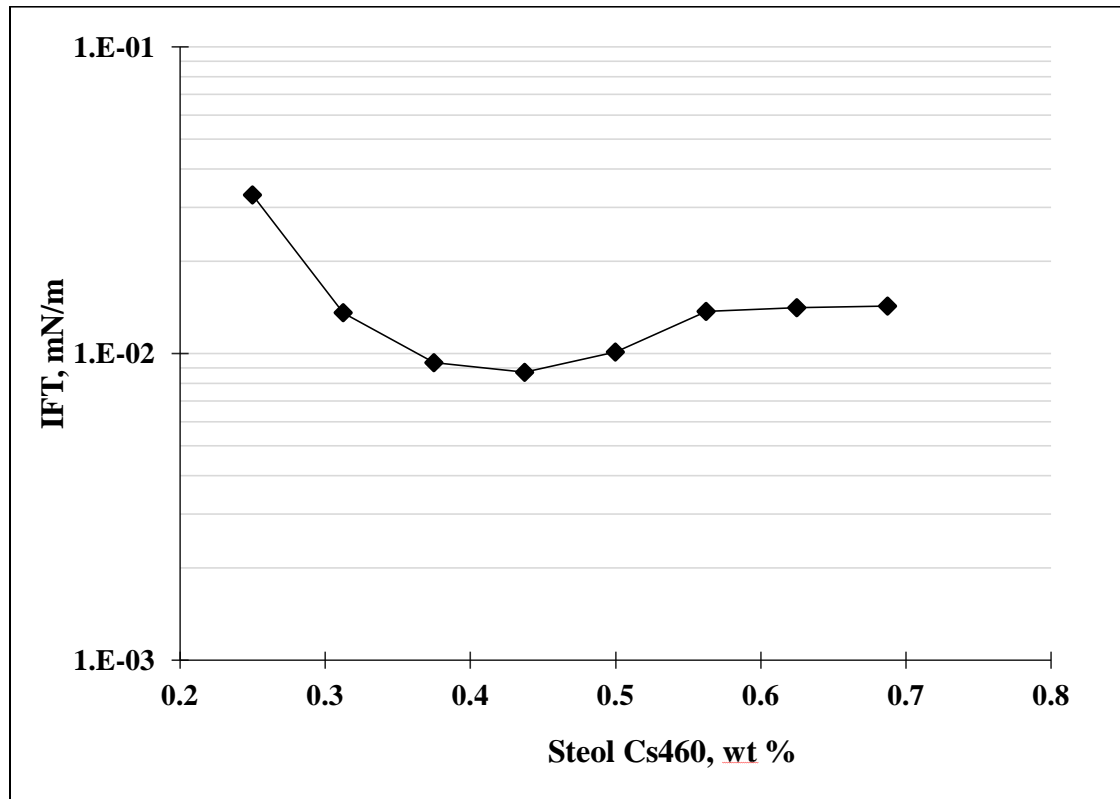


Figure 1.8. Equilibrium IFT measurements of the binary mixtures ($C_8-(PO)_4-(EO)_1-SO_4Na$, 0.25 wt % + SAES) with the reservoir crude oil at $52^\circ C$

1.3.2. Sand Pack Studies

Sand pack studies are conducted in laboratory for the purpose of optimizing the surfactant-only system for the field single-well flooding test. Figure 1.9 shows example of the sand pack study results involving the effect of varying total surfactant concentration (between 0.25 wt% to 0.75

wt%) on cumulative oil recovery. A glass column that is 1 inch in diameter and 6 inches long is used for sand pack studies. F-95 grade Ottawa sand is used as a column packing material. As seen in the Figure, decreasing the overall surfactant concentration from 0.75 wt% to 0.50 wt% decreases the cumulative oil recovery from 60% to 48%. A further reduction in oil recovery is observed for 0.25 wt% surfactant concentration (i.e., decrease to only 37 % recovered). Also in Figure 1.9, early oil breakthrough is observed for the sand pack that is flooded with 0.75 wt% surfactant concentration slug compared to that of sand packs flooded with less concentrated surfactant slug. Figure 1.10 shows the position of oil bank in sand pack immediately after flooding with one PV of each surfactant slug. It is observed that the sand pack flooded with 0.75 wt% surfactant slug has relatively higher oil bank position than that of 0.50 wt% and 0.25 wt% surfactant slugs respectively.

In ideal case where the surfactant adsorption in porous media is minimal and if ultra-low IFT at the oil-water interface is the only oil recovery mechanism then lowering overall surfactant concentration while maintaining the optimal Type III region should not decrease the cumulative oil recovery or nor should it delay the oil breakthrough. However, the observation made in this study doesn't correspond to the ideal case. One potential explanation could be the severe surfactant retention in porous media by adsorption. In the literature it is reported that the oil recovery is sensitive to the amount of surfactant injected and the amount of surfactant required depends on the level of adsorption in porous media. In such case, 0.75 wt% surfactant slug is arguably the best among other two less concentrated surfactant slugs as most surfactants are available to effectively participate in oil recovery mechanism. It is also likely that 0.75 wt% slug traverses in porous media faster because of more surfactant availability even after adsorption to mobilize oil resulting in faster oil bank formation and ultimately leading to the early oil

breakthrough.

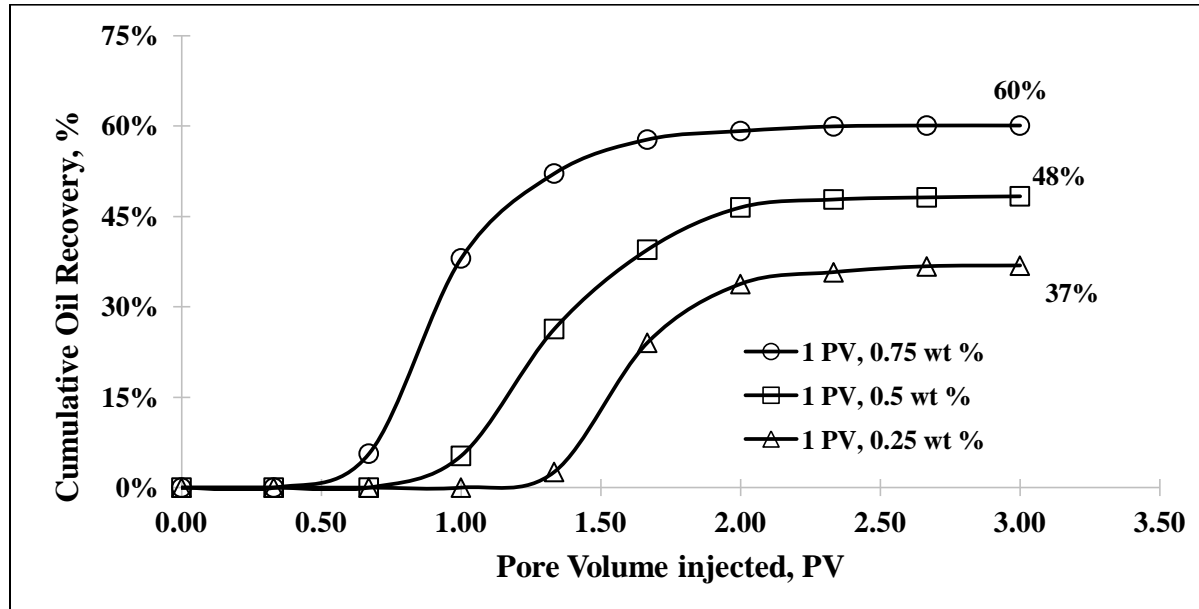


Figure 1.9. Effect of surfactant concentration on cumulative oil recovery and oil break through

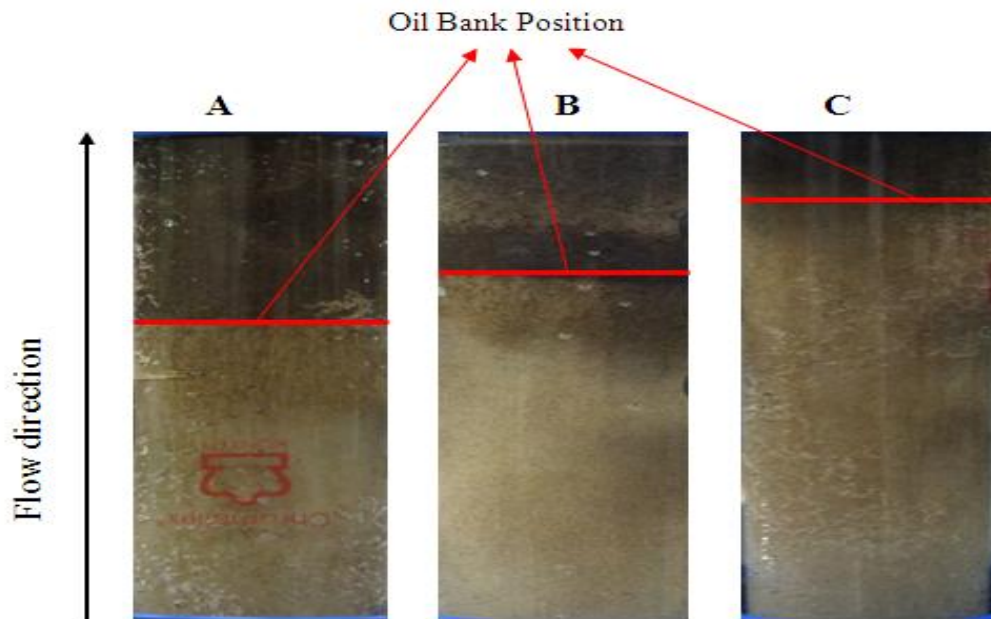


Figure 1.10. Sand pack studies: A. 1 PV, 0.25 wt% B. 1 PV, 0.50 wt% C. 1 PV, 0.75 wt%. Fluid injection rate: 0.3 ml/min

Table 1.7 summarizes the information of each sand pack test. Taking into account sand pack performance, field operation, and cost, the surfactant only flood system with slug size of 0.5 PV

and 0.5 wt % surfactant concentration is chosen as cEOR agent for field test. Literature shows that the sand pack test results correspond very well with coreflood test (Hsu et al., 2012). For this reason, coreflood tests are not performed in this study.

Table 1.7: Summary of sand pack studies

Sand Pack	Surfactant Injection protocol	IFT, mN/m	Initial Sor ± 0.02	Final Sor ± 0.02	Cumulative oil recovery, %
1	1 PV, 0.75 wt%	8.00E-03	0.24	0.1	60
2	1 PV, 0.50 wt%	7.80E-03	0.2	0.1	48
3	1 PV, 0.25 wt%	7.50E-03	0.26	0.16	37
4	0.50 PV, 0.50 wt%	8.1 E-03	0.23	0.14	41

1.3.3. *Equilibrium Partition Tracer Coefficient, K*

It is desired for a reactive tracer to have slightly higher solubility preference for oil over brine to estimate the Sor accurately. The equilibrium partition coefficient K of ethylformate measured in this study is 2.91 ± 0.30 . This value suggests that the ethylformate prefers oil almost 3 times to brine at the reservoir conditions. The K value, which is sensitive to the reservoir temperature, brine salinity, pH, and crude oil light component, is reported to be in the range of 2.0 to 8.0 (Deans & Carlisle, 1988; Jerauld et al. 2010).

Figure 1.11 shows the plot of ethylformate concentration versus time under the reservoir temperature. The slope of $\ln [EF]$ against Time (hr) in the study, $-0.284 \pm 0.03 \text{ hr}^{-1}$ ($7.88\text{E-}5 \pm 8\text{E-}6 \text{ s}^{-1}$), is the hydrolysis rate constant of the ethylformate. This value is similar to the rate constant, $7\text{E-}5 \text{ s}^{-1}$, reported in literature (Jin et al. 2015b) for ethylformate hydrolysis at the reservoir temperature of 123 °F.

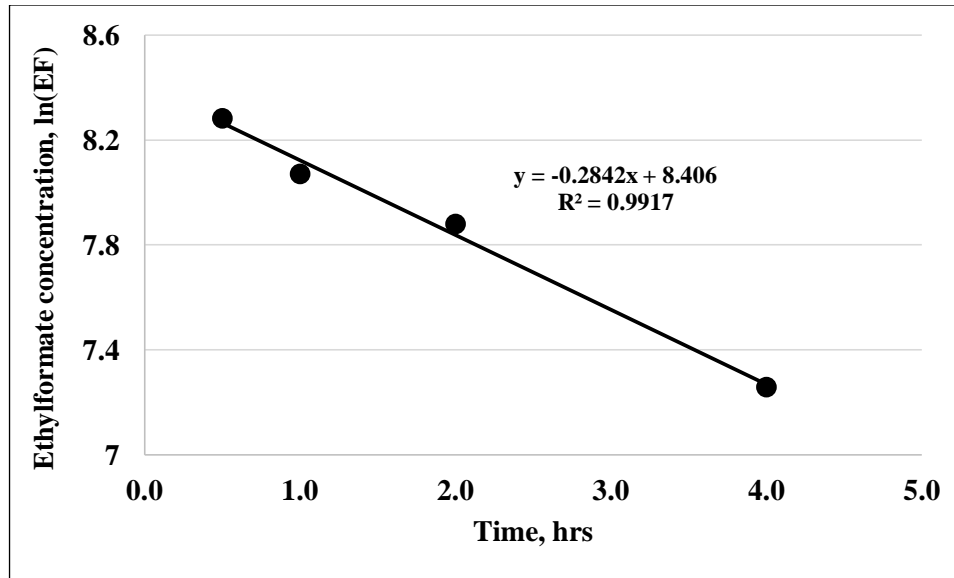


Figure 1.11. Ethylformate hydrolysis rate constant study

1.3.4. Field test results interpretation at W Site

The matched SWCTT results are shown in Figures 1.12 and 1.13 for pre and post surfactant injection respectively. The profiles of reactive tracer ethylformate and product alcohol ethanol are well fitted by a single layer model indicating a homogenous geological formation. Table 1.8 summarizes the fitting parameters. As observed in the table, the reaction rate of ethylformate decreases from $9.5 \times 10^{-5} \text{ s}^{-1}$ in pre surfactant SWCTT to $6.6 \times 10^{-5} \text{ s}^{-1}$ in post surfactant SWCTT. The decrease in rate constant is most likely the result of temperature drop from injecting high volume of cold fluid during the tests (Park et al. 1991). Similar phenomenon is also reported in literature (Jin et al., 2015).

The tracer concentration profile of pre surfactant SWCTT depicted in Figure 1.12 shows a narrow separation between the peaks of ethylformate and ethanol. This observation indicates that the S_{or} after water flooding is low (Deans & Carlisle, 1988) and is further confirmed from simulation results that shows water flooding S_{or} of 0.11. It is reported that based on reservoir formation, oil and brine properties, and other unknown variables, the S_{or} of mature reservoirs could vary from less than 0.1 to more than 0.45 (Deans & Carlisle, 1988). Given the fact that the War Party

formation is highly permeable, 500 mD to 1000 mD, it is possible for this specific reservoir to have S_{or} of 0.11, especially after being water flooded with 6 PVs of reservoir brine at three times higher injection rate than its equilibrium production rate of 55 bbls/day. Increasing the velocity of injection fluid increases the capillary number and thereby decreases the S_{or} (Stegemeier, 1974). Furthermore, as observed in Figure 1.13, there is no significant separation between the peaks of ethylformate and ethanol in post surfactant SWCTT indicating that the S_{or} is very low. The simulation results verify this observation and show the post surfactant S_{or} of 0.03.

An overall S_{or} reduction of about 73 % is observed after cEOR in field test, which is slightly higher, compared to the sand pack studies conducted with similar surfactant only injection protocol. However, sand pack studies are only used as a fast pre-screening tool for laboratory designed formulation and its resemblance to the actual reservoir is almost impossible. Jin et al. (2015) have also reported higher S_{or} reduction in field test compared to sand pack tests using surfactant only cEOR system.

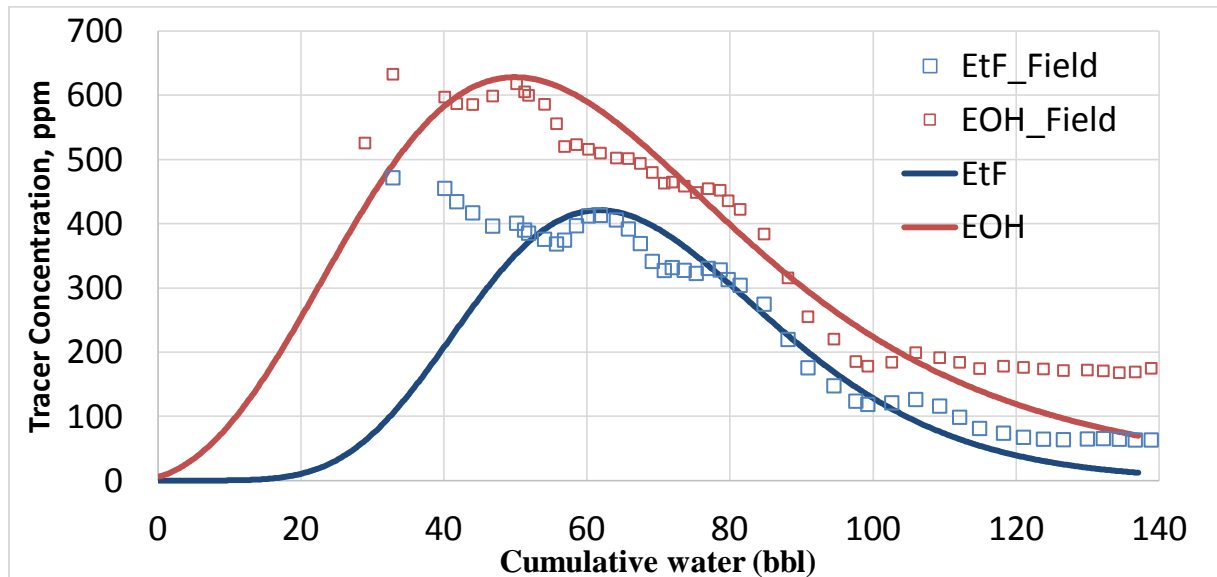


Figure 1.12. : Pre Surfactant SWCTT tracer concentration profile; single layer fitting

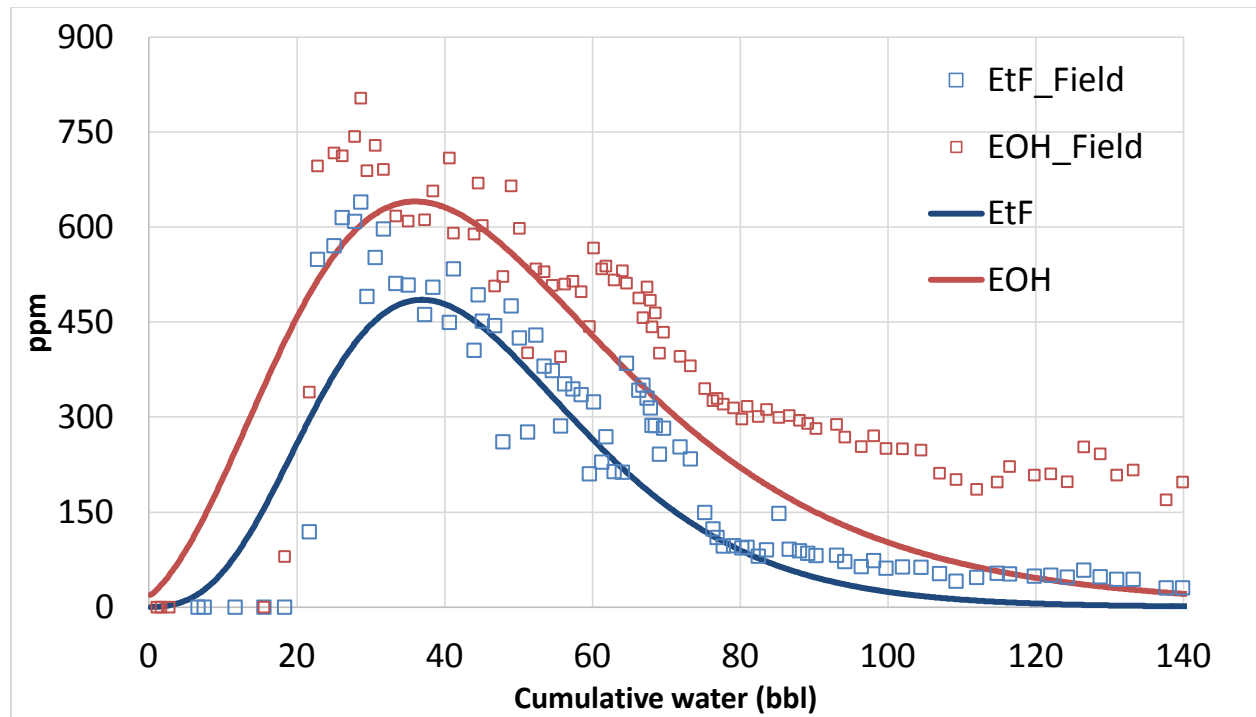


Figure 1.13. : Post Surfactant SWCTT tracer concentration profile; single layer fitting

Table 1.8. Simulation Matching Parameters

Matching Parameter	Pre Surfactant SWCTT	Post Surfactant SWCTT
Thickness (m)	3.66	3.66
Porosity	0.25	0.27
Partition Coef. K	2.91	2.91
Reaction Rate (s-1)	9.50E-05	6.60E-05
Sor = 1 - Sw	0.11	0.03
Dispersion Coef. Ethyl Formate	0.009	0.013
Dispersion Coef. Ethanol	0.009	0.03
Tracer Injection Rate (m3/day)	12.5	13.0
Pusher Injection Rate (m3/day)	27.5	19.0
Production Rate (m3/day)	24.65	22.0

1.3.5. Summary of W Site Test

Surfactant formulation developed for the ultra-high saline reservoir is optimized in laboratory through sand pack tests and is implemented in the field test at W site. Efficiency of the designed formulation in field is verified through SWCTTs and the numerical simulation is applied to interpret field data. Based on the results obtained, following conclusions can be made:

1. Surfactant formulation incorporating extended surfactant, $C_8-(EO)_1-(PO)_4-SO_4Na$, and SAES, $C_{12}-(EO)_3-SO_4Na$ shows excellent aqueous phase stability and generates ultra-low IFT of $8e-3$ mN/m with crude oil at the reservoir conditions.
2. Sand pack studies show improved cumulative oil recovery and early oil breakthrough with increased surfactant concentration. More surfactants available after reaching surfactant adsorption level to participate in oil recovery mechanism in the case of concentrated surfactant slug could be the potential explanation. Further study is recommended to understand surfactant only flooding systems better in sand packs.
3. The oil-water partition coefficient and hydrolysis rate constant of ethyl formate are determined in laboratory and are found to be 2.91 ± 0.30 and $7.88e-5 \pm 8e-6$ s⁻¹ respectively.
4. The reaction rate constant of ethyl formate is found to decrease from $9.5e-5$ s⁻¹ in pre surfactant SWCTT to $6.6e-5$ s⁻¹ in post surfactant SWCTT. Temperature drop due to high volume cold fluid injection along with pH drop due to product acid of ester reaction could have resulted such decrease in rate constant.
5. Highly permeable reservoir formation and high injection rate of water flooding could have resulted low Sor of 0.11 in pre surfactant SWCTT.

6. The Sor of 0.03 in post surfactant SWCTT and 73 % overall Sor reduction demonstrate that the laboratory optimized surfactant formulation is very promising and effective in mobilizing residual oil in ultra -high TDS reservoir.

1.4. Single Well Tracer Test at R site

1.4.1. Introduction

A Single Well Tracer Test (SWTT) was executed for the clients at the target R site on January of 2014 to assess the effectiveness of SWTT at this formation.

The test was conducted at the selected producing well EU in the R Field near Eastland, Texas.

The objective of the test was to determine residual oil saturation (Sor) and any further test and potential designing of viable EOR approaches would then be considered depending on the outcome of the tracer test results.

1.4.2. Testing Procedure and Field Results

The EU producer well at the R field was pre-screened and selected to be the test well for the Single Well Tracer Test (SWTT) based on the site characteristic and operations records. The EU well is completed to a depth of 3,429 ft with a perforated interval of 16 ft. The formation has an average porosity of 14.3% and a reservoir temperature of 120oF. The EU well produces approximately 150 barrels of total fluid per day. The radius of investigation was designed at 14' for the partitioning tracer and 19' for the non-partitioning tracer.

Prior to the test being conducted, a packer was set one joint above the perms. The packer is intended to isolate the flow of the injected fluids into the perforated interval and prevent entry of injection fluids into the annulus. During the week of the SWTT, the client shut-in the field, to eliminate potential reservoir influences.

Our group set up a portable field test unit at the field location on January 17, 2014.

Two 500 bbl frac tanks were placed on-site by the client. The frac tanks were filled with ~600 bbls of brine to be used for brine injection. The rod pump was unseated on January 18, 2014 at 2:30PM in preparation for the pre-flush to temporarily water out the test zone. A total of 500 bbls of brine was injected during the pre-flush at an average rate of ~750 bpd on vacuum. The injected brine was filtered with 1 micron size filter cartridges to prevent plugging of the formation. Injection rate and volumes were recorded during this procedure.

Prior to chemical tracer injection, the rod pump was temporarily reseated and produced back for 4 hours recovering approximately 42 bbls on Sunday, January 19th. This step cleans the perforations and helps ensure a good tracer push into the formation. The produced fluids from this 4 hour production period went into the north frac tank. The pump was then unseated for chemical tracer injection the following morning. Additional fresh water was delivered the afternoon of January 19th to provide the required fluids for tracer injection.

Chemical tracer injection started at 8 AM on January 20, 2014. Initially 62 bbls brine containing the reactive tracer (EtF), the cover tracer (NPA), and the mass balance tracer (MeOH) were injected. The concentrations of the tracers were: 10,432ppm for EtF, 4,365 ppm for NPA, and 3,342 for MeOH. This was followed by the push slug of 244 bbls of brine containing 3,342 ppm MeOH. The injection rate was held between 720-750 bpd on vacuum. During injection, the tracer solution was sampled and analyzed for tracer concentration by gas chromatography (GC).

The well was then shut-in for a two day soak period (January 21st and 22nd), during which the EtF hydrolyzed to form Ethanol (EtOH), the product tracer. At the conclusion of the soak period, the EU well pump was reseated for the pullback production stage on January

23rd. A total of 398 bbls were produced back over a two day period ending January 25th at 6AM. The produced fluid was sampled every 10 to 20 minutes for the first 960 minutes and every 30 minutes for the remainder of the test, a total of 2,850 minutes. Samples were analyzed for tracer concentration by GC on site.

The resulting chemical tracer profiles are shown in Figures 1.14 - 1.16 and are plotted as tracer concentrations vs. produced bbls. The ethanol product tracer, EtOH, is plotted against the NPA cover tracer in Figure 1.14. The primary reactive tracer, EtF, is plotted in Figure 1.15 along with the cover tracer, NPA. The material balance tracer, MeOH, is shown in Figure 1.16. The horizontal separation between EtOH and NPA tracer profiles in Figure 1.14 is the basis for determining the residual oil saturation using the SWTT method.

Figure 1.14. Concentration of EtOH versus Produced Volume for the SWTT

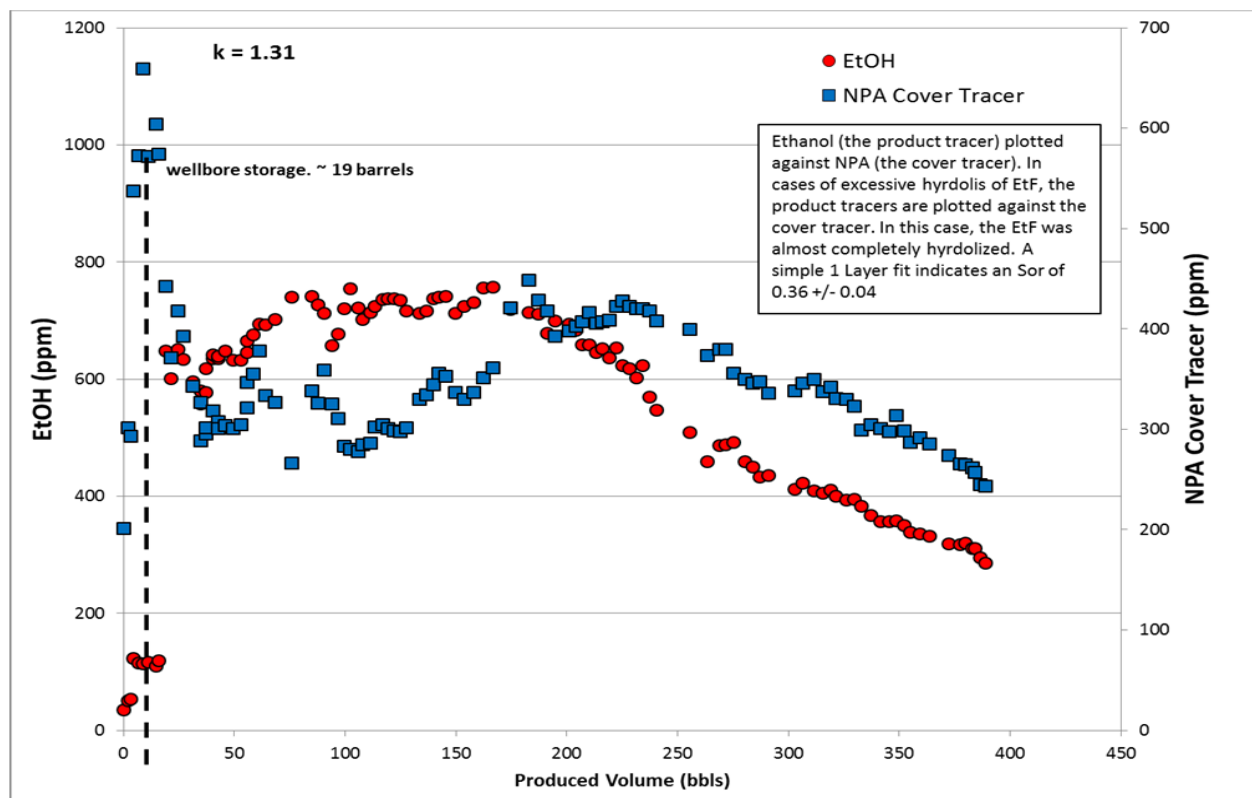


Fig. 1.15. Concentration of EtF versus Produced Volume for the SWTT

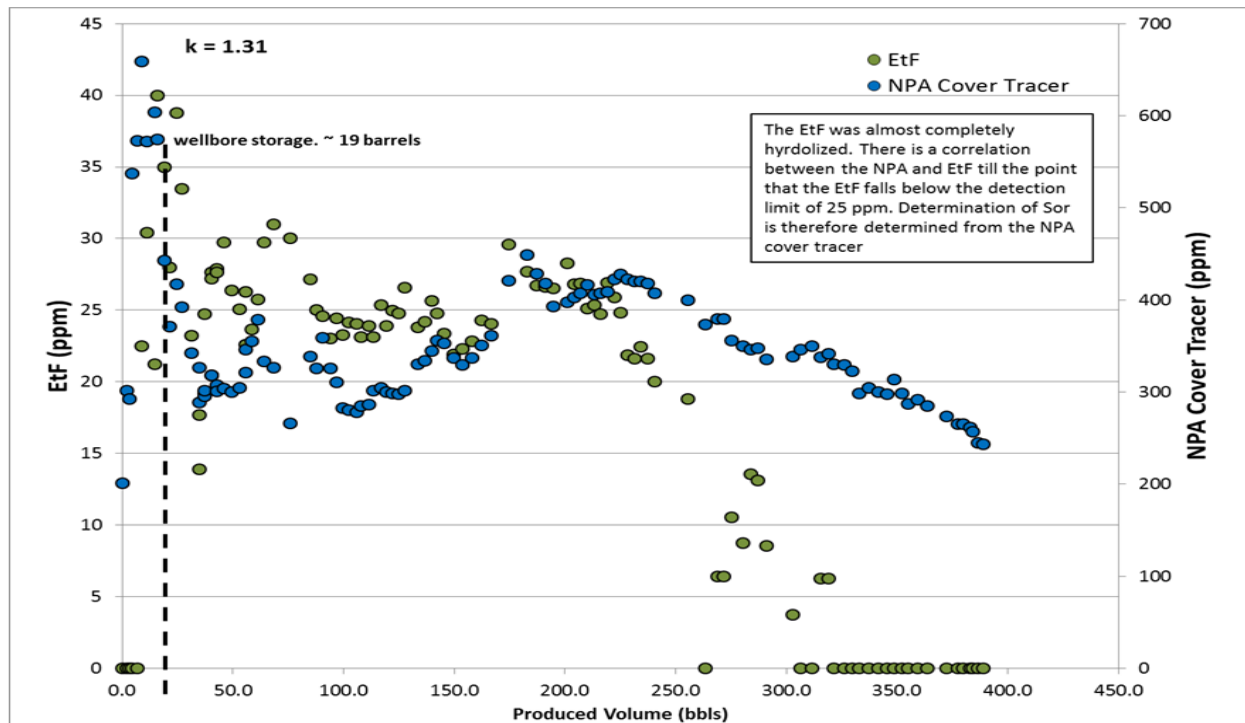
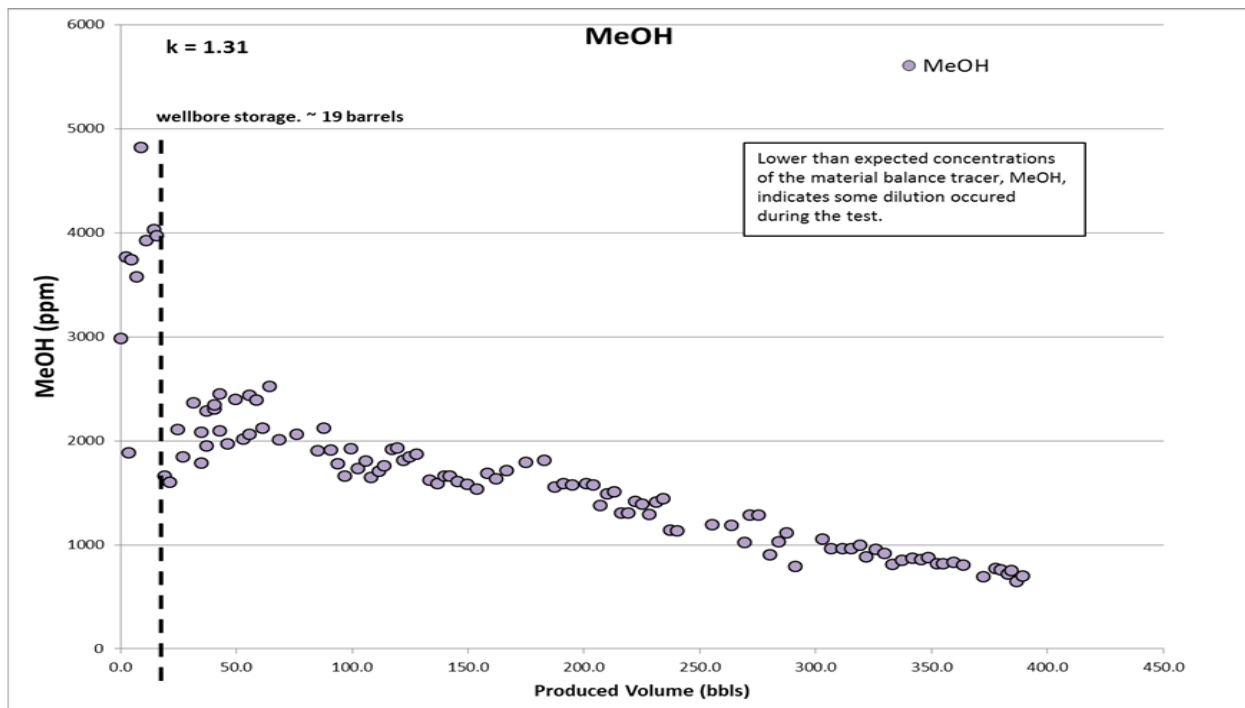


Fig. 1.16. Concentration of MeOH versus Produced Volume for the SWTT



1.4.3. Results of Single Well Tracer Test

Total tracer recovery was consistent between the mass balance tracer (MeOH) and cover tracer (normal propyl alcohol, or propanol, NPA) of 56% and 52%, respectively. Total ethanol, EtOH, recovery indicates 43% of the EtF was hydrolyzed. However, total EtF recovery was only 1.1%.

The results showed good separation between ethanol (EtOH) and the cover tracer NPA indicating detectable levels of Sor. In this case, higher than normal hydrolysis rates coupled with ~45% dilution resulted in very low recovery of the reactive tracer (EtF) even with a short soak period of only two days (typically, we use a three day soak period). Therefore, the cover tracer NPA was used as a substitute to determine Sor. In cases where there is not excessive drift, the cover tracer and EtF concentration profiles will closely match.

High measured levels of EtF, NPA, and EtOH during the first 50 bbls of production indicate irreversible flow. Some tracer entered portions of the formation during injection of the ester bank, but were not pushed out into the formation during subsequent slug push. After 50 bbls production, the tracer profiles contain EtOH and NPA peaks with well-defined leading and trailing edges.

Ideally, the mass balance tracer (MeOH) should be produced at the injected concentration of 3,342 ppm for the first 20 to 30 bbls before reflecting dispersion and slowly tapering down to about 800 ppm after 350 bbls produced. However, after the wellbore volume was recovered, the MeOH concentration dropped to 2,400 ppm indicating dilution. This dilution is indicative of a zone associated with the perforations that does not accepted tracer carrying water during injection but produces water during production.

Determination of residual oil, Sor, was made with the updated partition coefficient of $K = 1.31$

(the partition coefficient was analyzed post the test using injected brine samples taken at the site). The partition coefficient of the ester tracer (EtF) and oil saturation encountered by the ester determines how much slower the ester returns to the well than the product alcohol. The time separation between the slower moving retained tracer, the ester, and the more quickly moving produced tracer, the product alcohol, is directly related to oil saturation. In this case, the NPA cover tracer was substituted for the ester tracer.

The EtOH and NPA profiles are well defined and S_{or} is readily measured. Determination of S_{or} was performed by delineating the x-axis position of NPA and the corresponding x-axis position of EtOH (see basic equation below for determination of S_{or}). These positions were quite easy to match. The best-fit flow model that matched the NPA and EtOH profiles is a radial flow model (see below).

$$S_{or} = \frac{((Q_a - \delta)/(Q_b - \delta)) - 1}{((Q_a - \delta)/(Q_b - \delta)) - 1 + K}$$

δ wellbore storage in bbls
 Q_a produced volume at NPA peak
 Q_b produced volume at EtOH peak
 K partition coefficient

Where,

Q_a produced volume at NPA peak

Q_b produced volume at EtOH peak

K partition coefficient

A single layer model was used to fit the NPA and EtOH profiles and is likely the best indication of S_{or} (see modeled profiles in Figure 1.17). Figure 1.18 is the modeled profile for the MeOH mass balance tracer. The estimated S_{or} was $\sim 0.36 \pm 0.04$ (see Table 1.10). The uncertainty of ± 0.04 was due to indications of dilution, irreversible flow, as well as injection of fresh water

during chemical tracer injection. A sensitivity analysis of S_{or} to the partition coefficient is given in Table 1.9.

Table 1.9. Sensitivity analysis of S_{or} against various K

Wellbore Storage (bbls)	19
Q_a (bbls)	229
Q_b (bbls)	141
K	1.31
B	0.72
S_{or} (frac)	0.36

$K = 1.10$	0.40
$K = 1.20$	0.38
$K = 1.31$	0.36
$K = 1.40$	0.34
$K = 1.50$	0.32

Fig. 1.17. EtOH concentrations of measurements and simulated data against the produced volume

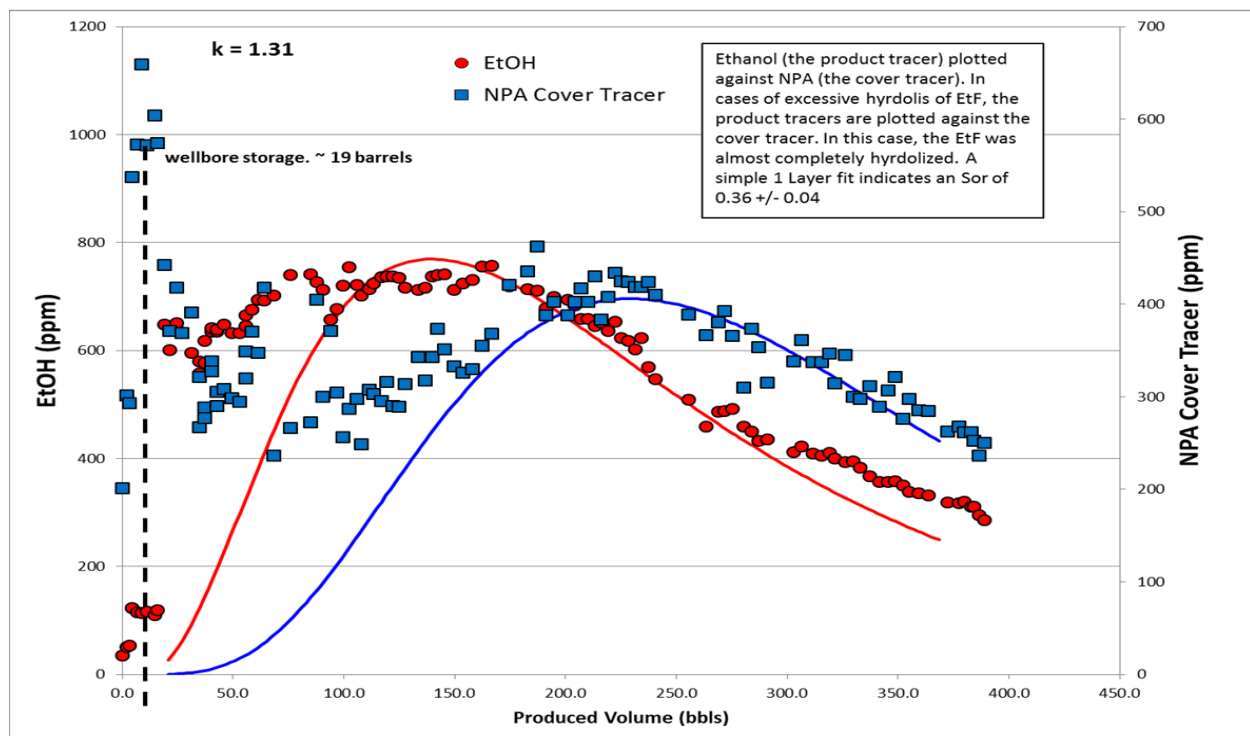


Fig. 1.18. MeOH concentrations of measurements and simulated data against the produced volume

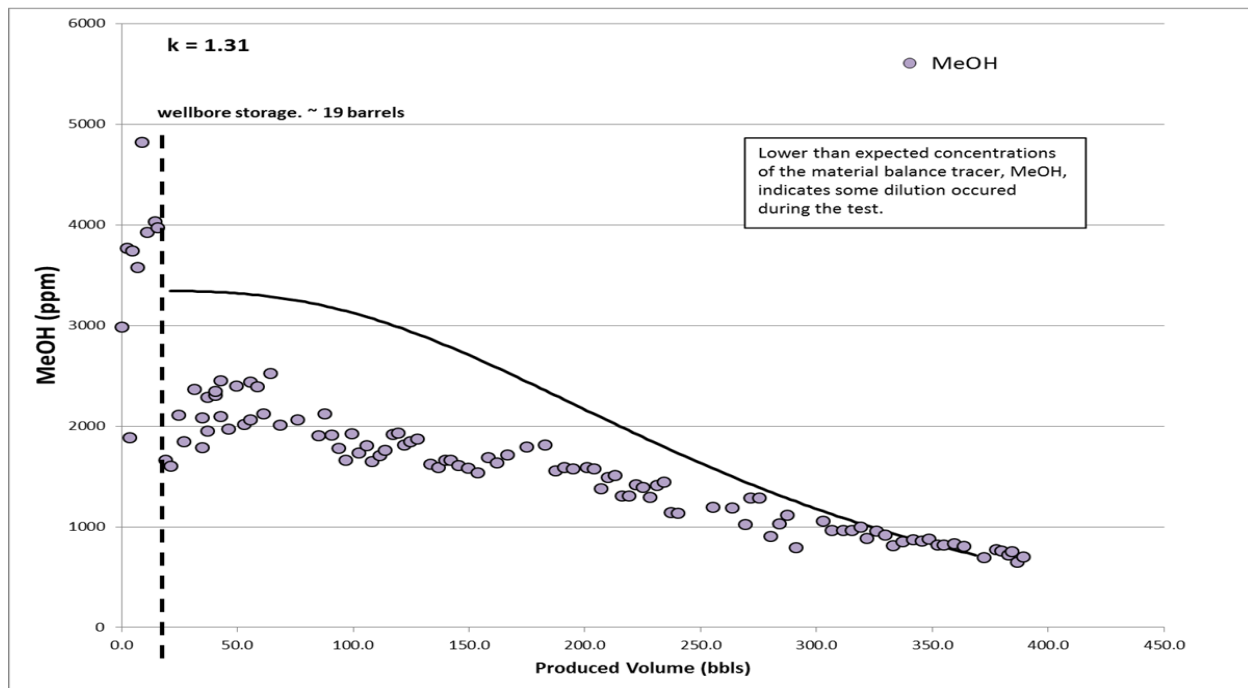


Table 1.10. Summary of estimated Sor at EU well of R Site

Well Name	Measured Sor (frac)	Uncertainty (frac)
EU well	0.36	0.04

1.4.4. Summary of Single Well Test at R site

The test showed good profile definition of the product tracer (ethanol, EtOH) and cover tracer (propanol, NPA). The separation in arrival times of EtOH and NPA indicates good sensitivity to Sor.

Unfortunately, due to high hydrolysis rates and dilution of the tracers, very little of the reactive ester tracer (ethyl formate, EtF) was recovered and, as such, the NPA cover tracer was substituted in the determination of Sor. Ideally, the SWTT would be modified to shorten the

shut-in time to improve the data interpretation. Yet, this modification could not be realized due to the site and budget limitations.

Thus, the S_{or} was determined by delineating the x-axis position of the NPA and the corresponding position of the EtOH. The measured S_{or} is 0.36 ± 0.04 within the reservoir pore volume penetrated by the tracer carrying fluid. Details of the test are given below along with a discussion of the results and findings.

Further tests at R site have not been decided by the client based on the results of pre-chemical flood tracer test. No further action would be taken at the R site.

1.5. Mini-Single Well Tracer Test at AB Site

A mini-single well tracer was conducted at the AB site (a Red Fork Formation located in Oklahoma) based on preliminary tracer tests indicating significant drifting phenomena might occur near the target well impacted by surrounding active producing wells. Preliminary results of tracer test indicated that significant tracers mass injected were not counted during the pull-back operations.

1.5.1. Objective

The aim of the mini-test was to evaluate the drift rate in the formation at AB Site (Well #15) which could potential impact the data interpretation of tracer recovery and the estimated S_{or} .

1.5.2. Procedures

In general, the injection protocols called for the mini tracer test involves injection of a smaller slug of tracer(s) into the formation, with a brief of shut-in time (i.e., last only few hours), and resume the pumping and recover the injected tracers from the formation. Specifically, at the AB site, the pre-determined chemical slug of the mini test and injection and recovery steps included

the following based on documentation of prior literatures,

- a. Step 1. Injection of 15 bbls of 1% MeOH solution (3.5 hours)
- b. Step 2. Injection of 15 bbls of 1% PrOH solution (3.5 hours)
- c. Step 3. Injection of 30 bbls of brine (7 hours)
- d. Shut-in 5 hours
- e. Production: 28 hours
- f. Sampling protocol (for GC analyses)
 - During injection: once every 1 hour
 - During production: once every 10 minutes

The advantages of mini test are that it is rapid, easy to conduct, low cost with the benefits of retrieving field data indicating the integrity of well bore and existing hydrodynamic conditions with much quicker time frame, as compared to conventional single well test. This is especially true for an unknown mature field which may largely lack comprehensive operation records and additional tests been conducted in the past and/or in some cases, the integrity of well and the flow field might be questionable.

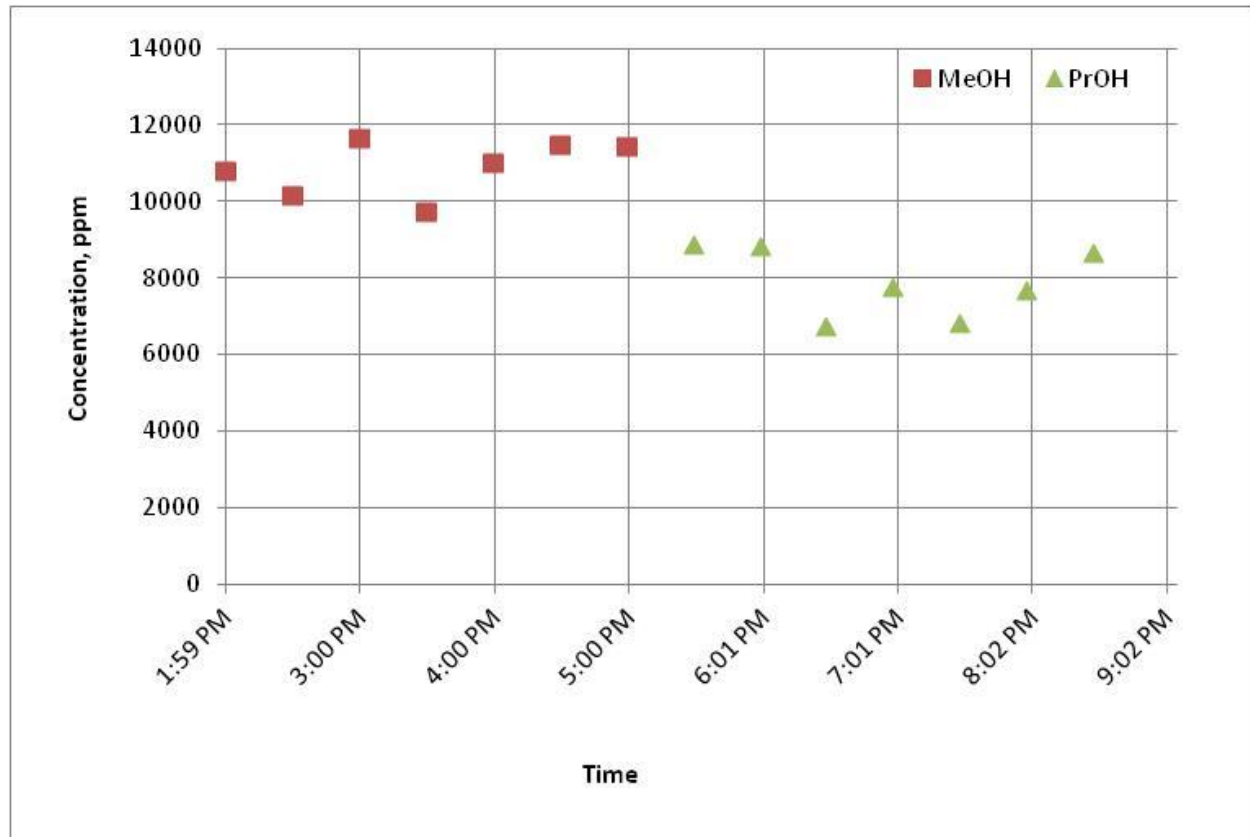
1.5.3. Results of Mini Test at AB Site

Total amounts of tracer concentration used during the mini test are summarized in Table 1.11. Dual alcohols (methanol and NPA) were used in this test, and both were non-reactive (i.e., conservative, or non-partitioning). Results of tracer concentration injected during the injection stages are shown in Figure 1.19.

Table 1.11. Tracer concentration injected

	MeOH	PrOH
Average injected concentration, ppm	10906.8	7928.9

Fig. 1.19. MeOH and NPA Concentrations versus injection time



Results of tracer concentrations during production step and the average production rate are depicted in Figures 1.20 and 1.21, respectively. Based on these recovered concentrations and flow rates (Figs. 1.19 – 1.21.), the total amounts of alcohols injected and recovered in the test were calculated and summarized in Table 1.12.

Table 1.12. Material balance of the tracers injected

	MeOH	PrOH
Total Recovered, kg	14.22	9.34
Total injected, kg	29.07	18.22
% recovery	48.91	51.27

Fig. 1.20. Concentrations of MeOH and NPA versus production time

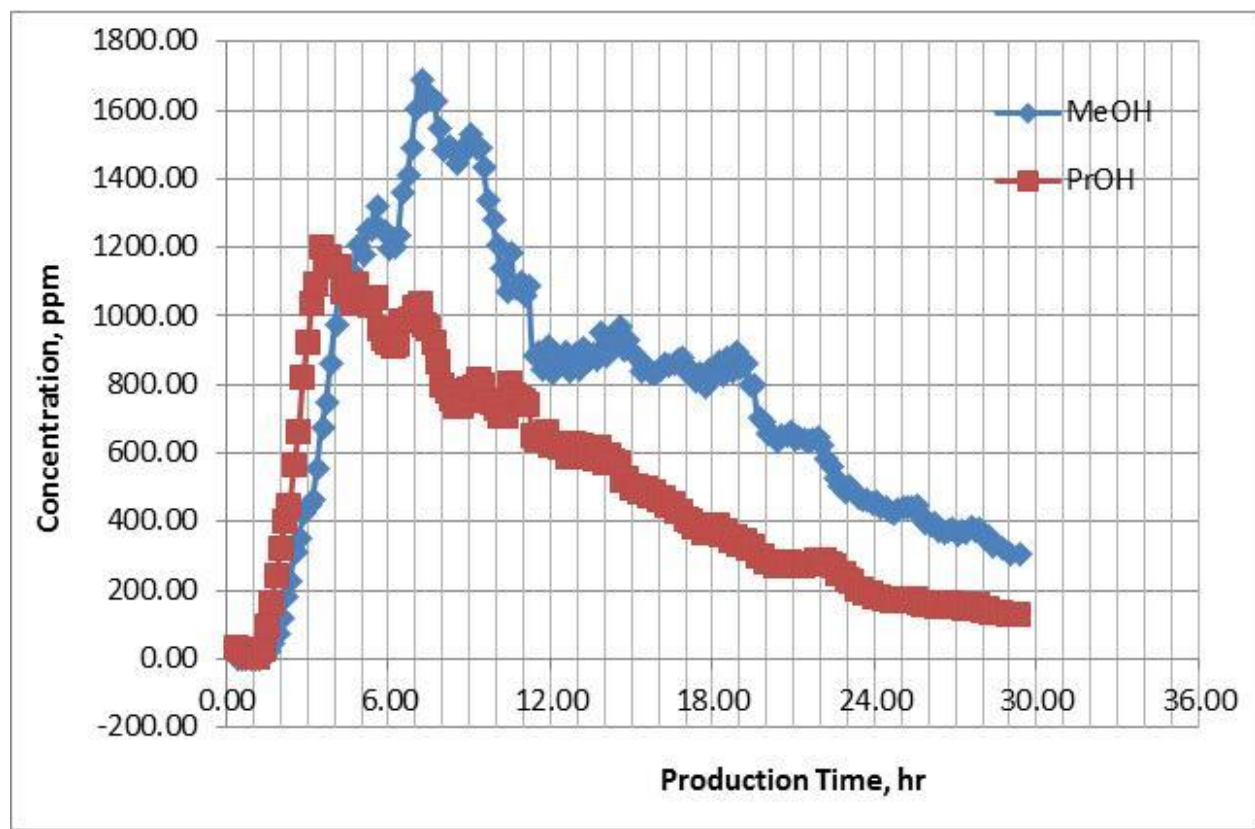
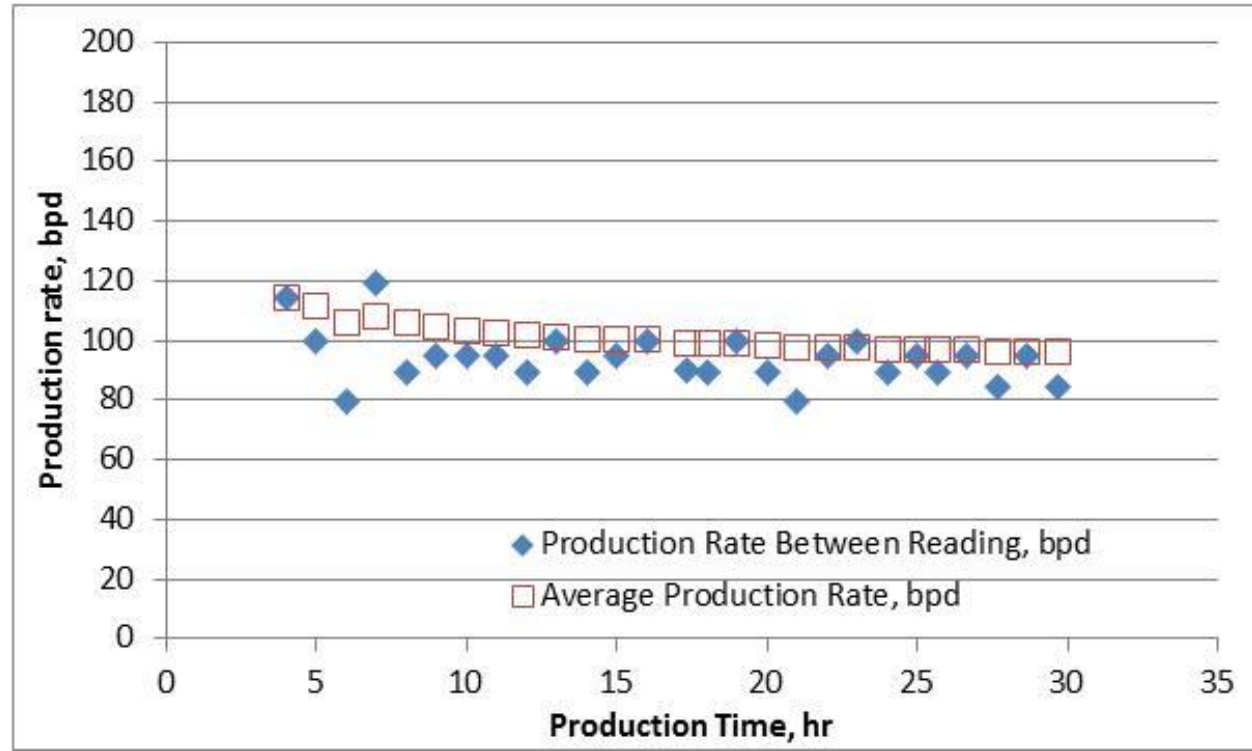


Fig. 1.21. Cumulative production rate and average production against time



To facilitate the estimation of the drift (as denoted as parameter, d), we used the following approaches as shown in Figures 1.22 – 1.23. The assumptions are formation permeability being constant and homogeneous, no leak at the wellbore. Based on the mass of MeOH and PrOH recovered and actual production rate, results of drift (estimated) were summarized in Tables 1.13 and 1.14. The resulted drift rates of MeOH and PrOH were 57.5 ft/d and 58.5 ft/d, respectively. We also compared the estimated draft rates for several prior SWTT sites conducted by this group at various formations and the results were summarized in Table 1.15. The mini test at AB site indicated that we had much higher draft at this location.

Fig. 1.22. Maps of tracer migration and radius of plume

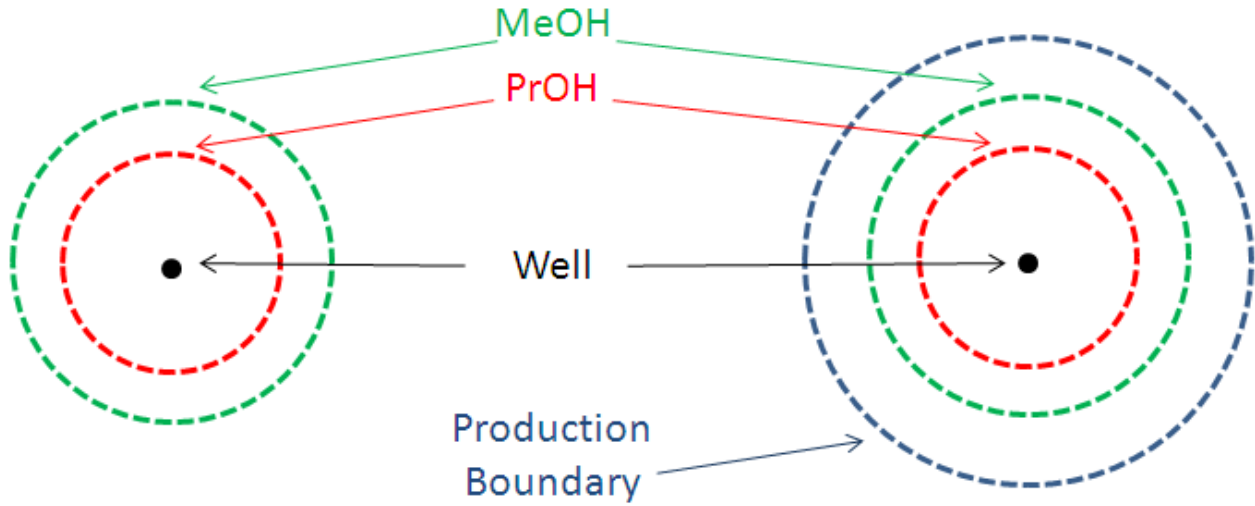
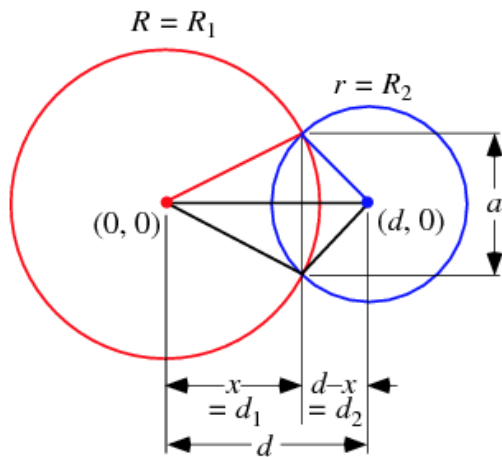


Fig. 1.23. Formulation and calculation for the intersected area between the tracer plume and production boundary



$$A = r^2 \cos^{-1} \left(\frac{d^2 + r^2 - R^2}{2 d r} \right) + R^2 \cos^{-1} \left(\frac{d^2 + R^2 - r^2}{2 d R} \right) - \frac{1}{2} \sqrt{(-d + r + R)(d + r - R)(d - r + R)(d + r + R)}.$$

where:

A is the intersected area between two circles (known: tracer mass balance)

d is the distance between two circles (unknown)

R is the radius of the circle #1 (known: production radius)

r is the radius of the circle #2 (known: tracer circle)

Fig. 1.24. Intersected area estimated for PrOH (red) MeOH (green)

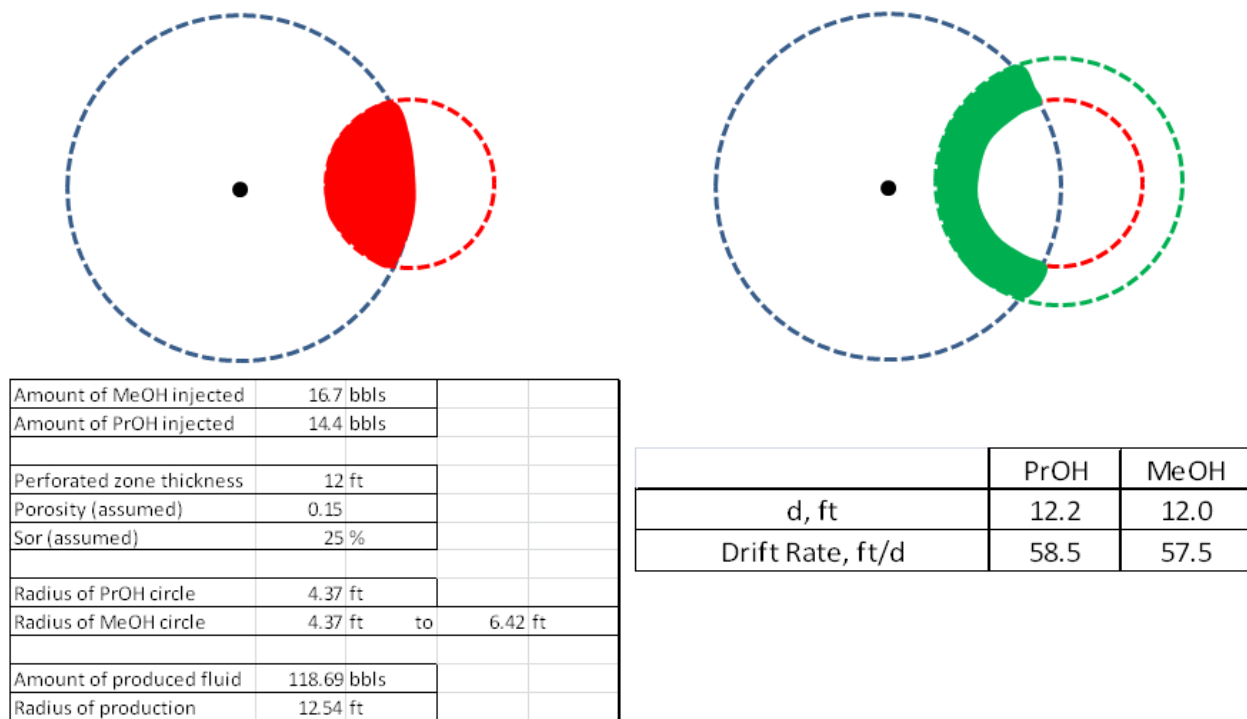


Table 1.13. Parameters used in drift calculation **Table 1.14.** Results of d & drift rates

Table 1.15. Comparison of drift rates at different formations and wells

Site	Drift Rate, ft/d	
	PrOH	MeOH
M 29 Pre-ChemFlood SWTT	4.76	n/a
M 29 Post-ChemFlood SWTT	6.56	6.37
SF 56 Pre-ChemFlood SWTT	6.74	6.15
SF 56 Post-ChemFlood SWTT	10.13	10.01
AB 18 Pre-ChemFlood SWTT 1 st	7.04	7.54

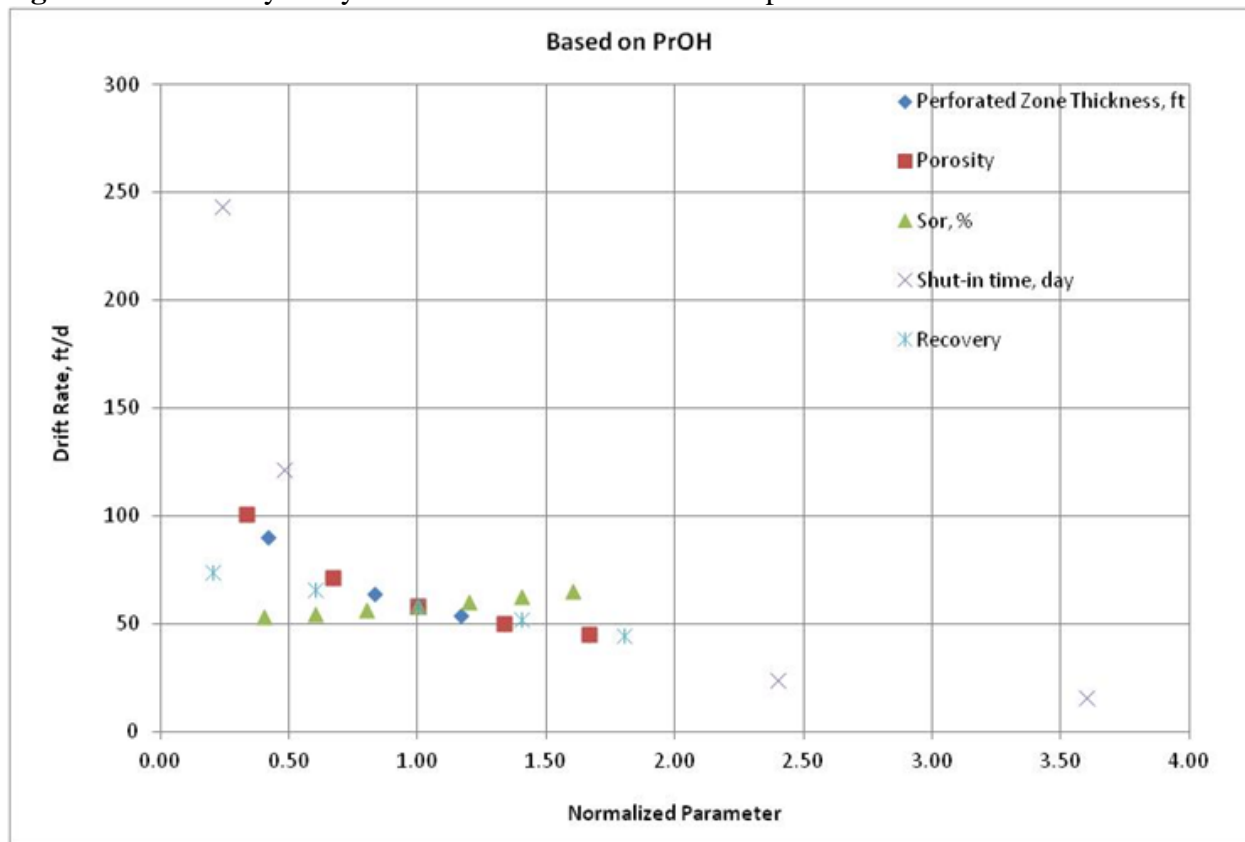
AB 18 Pre-ChemFlood SWTT 2 nd	9.25	9.50
AB 15 Pre-ChemFlood SWTT 1 st	7.97	8.01
AB15 Pre-ChemFlood SWTT 2 nd	5.59	5.80
AB 15 Pre-ChemFlood minitest	58.5	57.5

We also conducted the sensitivity analysis on drift rate calculation based on various parameters, such as perforated zone thickness, porosity, Sor, shut-in time , and % mass recovery. The results are depicted at Table 1.16 and Figure 1.25. While most parameters showed some extent of affecting the drift rate, the levels of Sor show negligible impact on the drift rate, and change of the shut-in time pose most significant impact on the drift.

Table 1.16. Summary of sensitivity analysis on drift rate

Perforated Zone Thickness, ft	Normalized Parameter	Drift Rate, ft/d		Shut-in time, day	Normalized Parameter	Drift Rate, ft/d	
		PrOH	MeOH			PrOH	MeOH
5	0.42	90.6	89	0.05	0.24	243.8	239.4
8	0.67	71.6	70.3	0.1	0.48	121.9	119.7
10	0.83	64.1	62.9	0.21	1.00	58.5	57.5
12	1.00	58.5	57.5	0.5	2.40	24.3	23.9
14	1.17	54.2	53.2	0.75	3.60	16.2	16.9
16	1.33	50.6	49.7	1	4.80	12.1	11.9
20	1.67	45.3	44.5	2	9.60	6	5.9
Porosity				3	14.40	4	3.9
0.05	0.33	101.3	99.5	Recovery			
0.1	0.67	71.6	70.37	0.1	0.20	73.97	80.06
0.15	1.00	58.5	57.5	0.3	0.60	65.8	67.7
0.2	1.33	50.6	49.7	0.5	1.00	58.5	57.5
0.25	1.67	45.3	44.5	0.7	1.40	52.3	47.7
Sor, %				0.9	1.80	45	37.3
10	0.40	53.4	52.4				
15	0.60	54.9	53.9				
20	0.80	56.6	55.6				
25	1.00	58.5	57.5				
30	1.20	60.5	59.4				
35	1.40	62.8	61.7				
40	1.60	65.4	64.2				

Fig. 1.25. Sensitivity analyses of drift rate versus different parameters



We also assessed the effect of sampling frequency (most samples collected at 10 mins during the mini test) and the results are shown in Figures 1.26 – 1.27 for PrOH and MeOH, respectively.

Effects of sampling frequency on recovery and peak location are depicted in Table 1.17. Results of tracer breakthrough indicated sampling frequency between 10 to 30 mins provides reasonable close data of recovery and peak location. Increase of sampling frequency to 60 mins would tend to increase the uncertainty on the data interpretation and deviate from the actual values of the retrieved samples.

Fig. 1.26. Results of PrOH concentrations at different sampling frequency versus production time

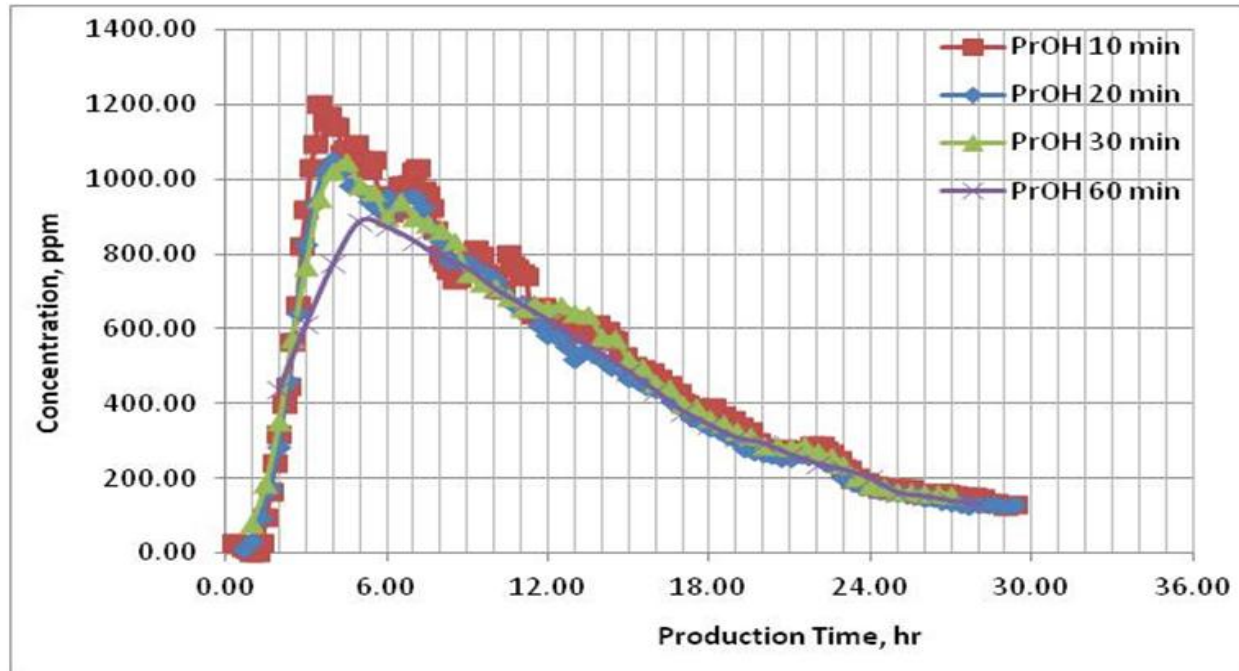


Fig. 1.27. Results of MeOH concentrations at different sampling frequency versus production time

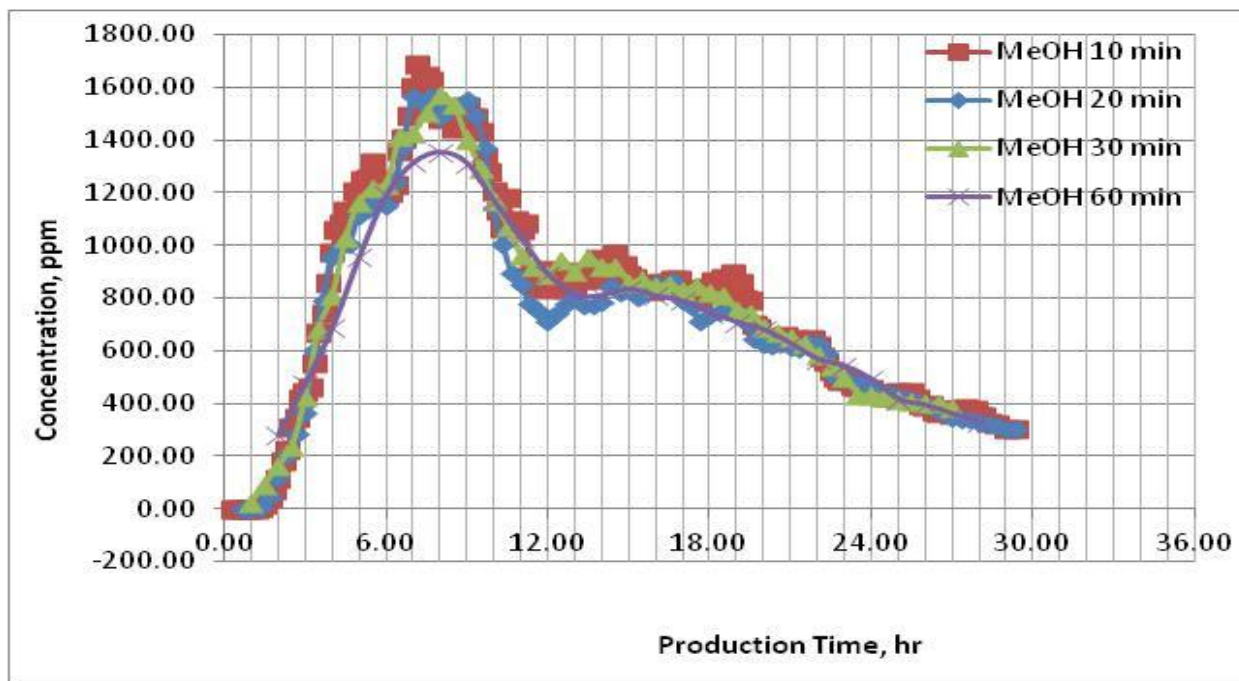


Table 1.17. Summary of sampling frequency on recovery and peak location

	MeOH				PrOH			
Sampling Freq., min	10.00	20.00	30.00	60.00	10.00	20.00	30.00	60.00
Total Recovered, kg	14.22	13.49	13.80	13.34	9.34	8.77	9.06	8.64
Total Injected, kg	29.07	29.07	29.07	29.07	18.22	18.22	18.22	18.22
% Recovery	48.91	46.39	47.46	45.89	51.27	48.12	49.73	47.41
Peak Location, hr	7.17	7.00	8.00	8.00	3.50	4.00	4.50	5.00

1.6. Pilot Interwell Chemical Flood Test at SK Site

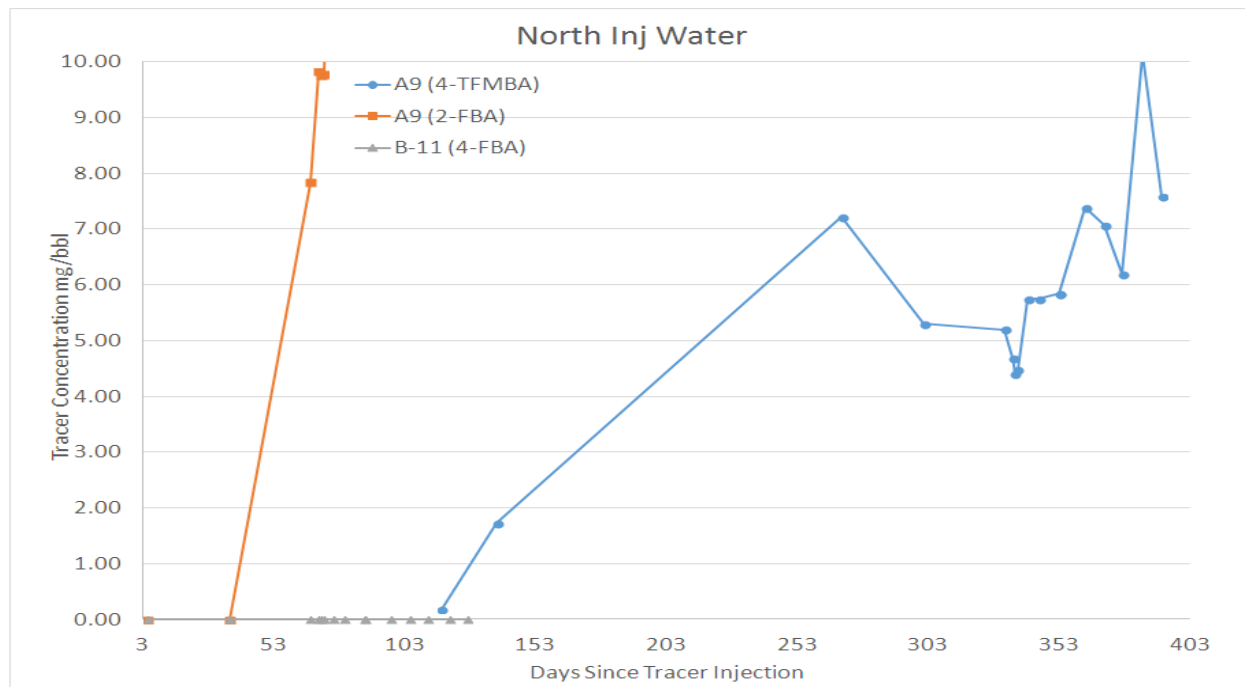
1.6.1. Aim:

Though our main endeavor of this study was to explore different approaches and designs of multiple single well tests for facilitating design of future pilot multi-well injection, our team also had the opportunities to conduct a quick pilot multi-well test at the SK site (near northeastern Oklahoma). Thus, the main aims of this quick inter-well test involving one injection and one production well were at least two folds: 1) to assess injection of the developed surfactant formulations and closely monitor the response of the chemicals injected at the production well, 2) based on these preliminary test and explore the opportunities of injecting surfactant-only system for enhancing oil recovery. Since this is a quick pilot inter-well test, the main tasks involved monitoring the injected tracer breakthrough, the breakthrough of chemicals injected and trend of oil recovery.

Several fluorobenzoic acids, 2-fluoro benzoic acid (2-FBA), 4-fluoro benzoic acid (4-FBA), 4-trifluoromethyl benzoic acid (4-TFMBA), were selected as inter-well tracers for the test and injection of these tracers at the target injection were conducted with sequential approach, injecting tracer 1 at Day 1 and followed by injecting tracer 2 at latter day, x. Once injected, monitoring of the tracers breakthrough were continuously taken place at the selected surrounding (producing) wells to better delineate the flow path of the target zone based on the history of

breakthrough and the level of peak tracer concentration using moment analysis. An example of tracer used and their breakthrough at near by producing well (North Inj Water well) at SK site was depicted at Figure 1.28. The fluorobenzoic acids were measured by GC with a MS detector with sampling pretreatment developed in-house at CFT. As shown in this figure, the connectivity between injection well A9 and producing well (North Inj Water) is reasonable good. However, the connectivity between wells B-11 and North Inj Water was poor as indicated by lack of any tracer breakthrough at North Inj Water within reasonable time frame based on the assumption of darcy law and average permeability of the formation. The shape of the breakthrough curves (see Figure 1.28) are somewhat different between two sequential tracers injected (2-FBA and 4-TGMBA), likely due to a modification of active production wells and their pumping rate and well pattern was taken place at the target area.

Fig. 1.28. Example of tracers used in the inter-well and their breakthrough



Results of several non-partitioning tracer tests conducted at the targeted well (PA4) are shown in Figures 1.29 and 1.30. The breakthrough of tracers between two separate tests are quite similar (see Figure 1.29); while Test 1 was conducted in 2012, Test 2 conducted in 2013. Based on the tracer breakthrough data (2-FBA in Figure 1.30), the breakthrough of conservative tracers at well PA 4 should be around 104 to 120 days, as confirmed by second tracer injected (4-TFMBA).

Fig. 1.29. Comparison of two separate tracer injection/breakthrough at the targeted well (PA4) at SK site (note that: test 2 was conducted few months before the surfactant injection)

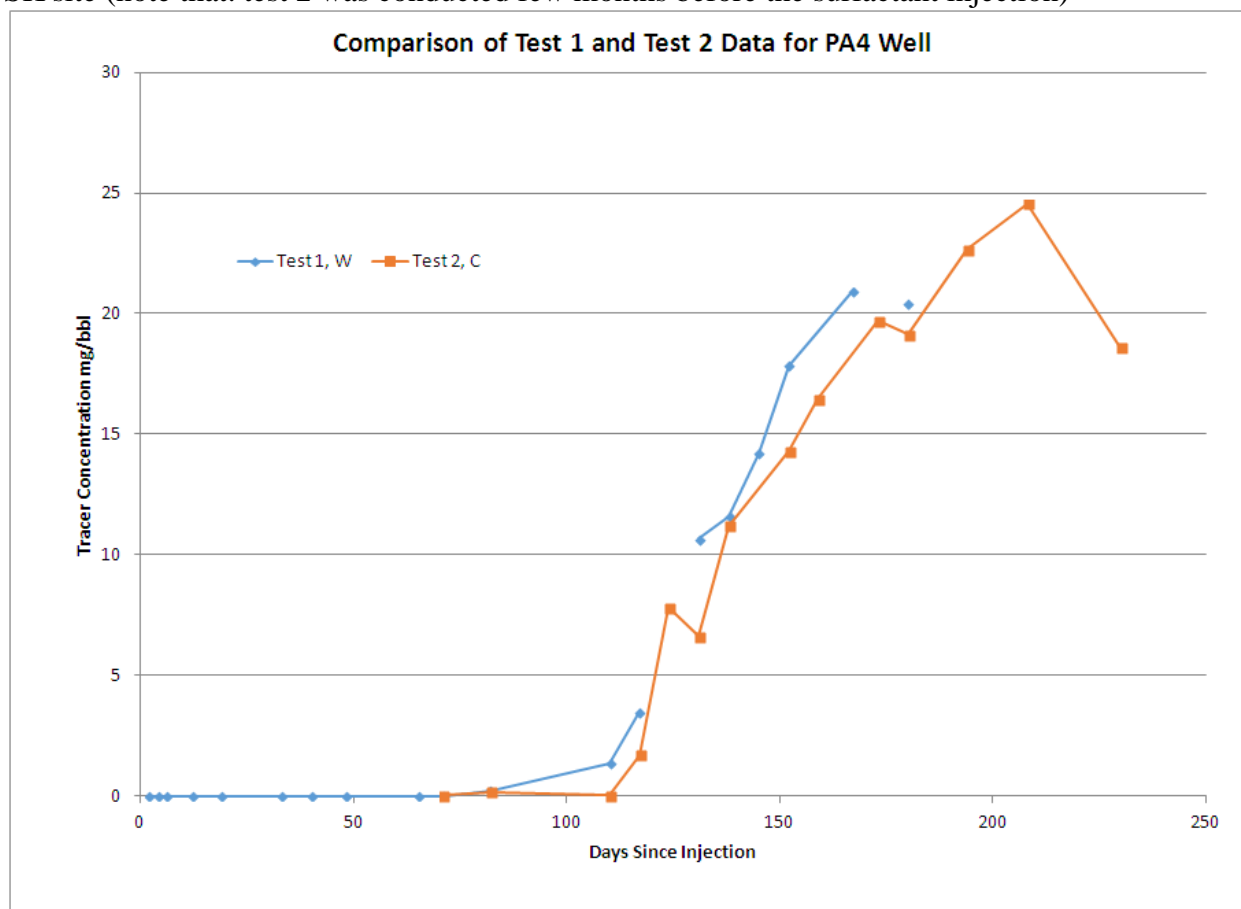
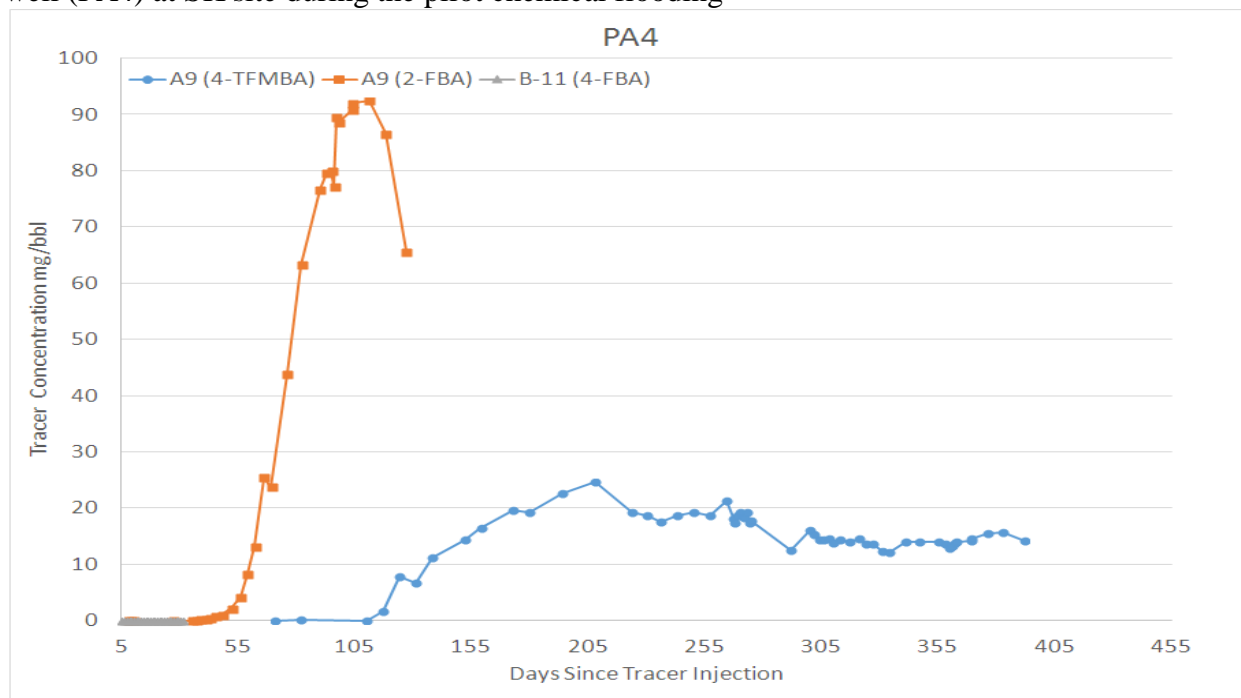


Fig. 1.30. Comparison of two sequential tracer injection (2-FBA & 4-TFMBA) at the targeted well (PA4) at SK site during the pilot chemical flooding



The developed surfactant formulations for the SK site was a mixture of dual surfactant system: Propoxylated alcohol sulfates (2560 mg/L) and ethoxylated alcohol sulfates (2450 mg/L) and other performance booster additives (a total of 1000 mg/L). The targeted PV of chemical slug was 0.75 PV (=15,000 bbls) (the total chemicals required = 6276 gallons based on the concentrations). The selected optimal surfactant solution was based on the laboratory batch experiments and core flood tests (with Berea core).

Injection of surfactant started at September 17th of 2013. The record of chemical injection are depicted in Figure 1.31. And the second non-partitioning tracer (2-FBA) was also injected to verify the flow path during the chemical flood as shown in Figure 1.32. Surfactant blend were prepared on site in 2000 gallon flexi tank per batch (see Figure 1.33). Overall, injection of surfactant mixture went well over the course the chemical flood stage. Example of produced sample collected is depicted in Figure 1.34.

Fig. 1.31. Injection of chemical (surfactant plus additives) at SK site

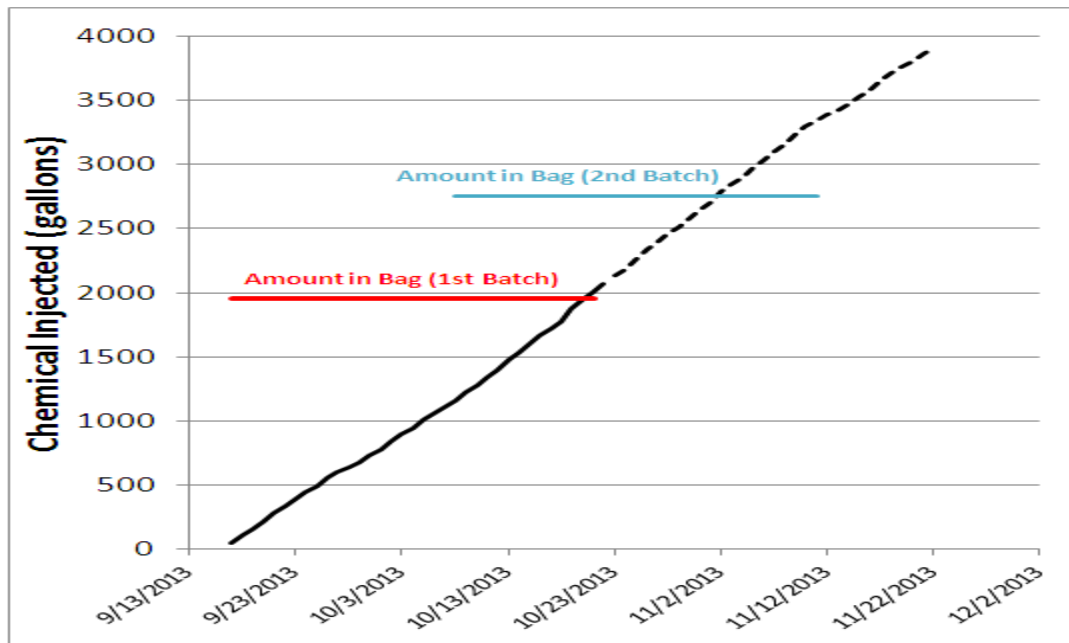


Fig. 1.32. Tracer concentration (2-FBA) and its breakthrough during the chemical flood

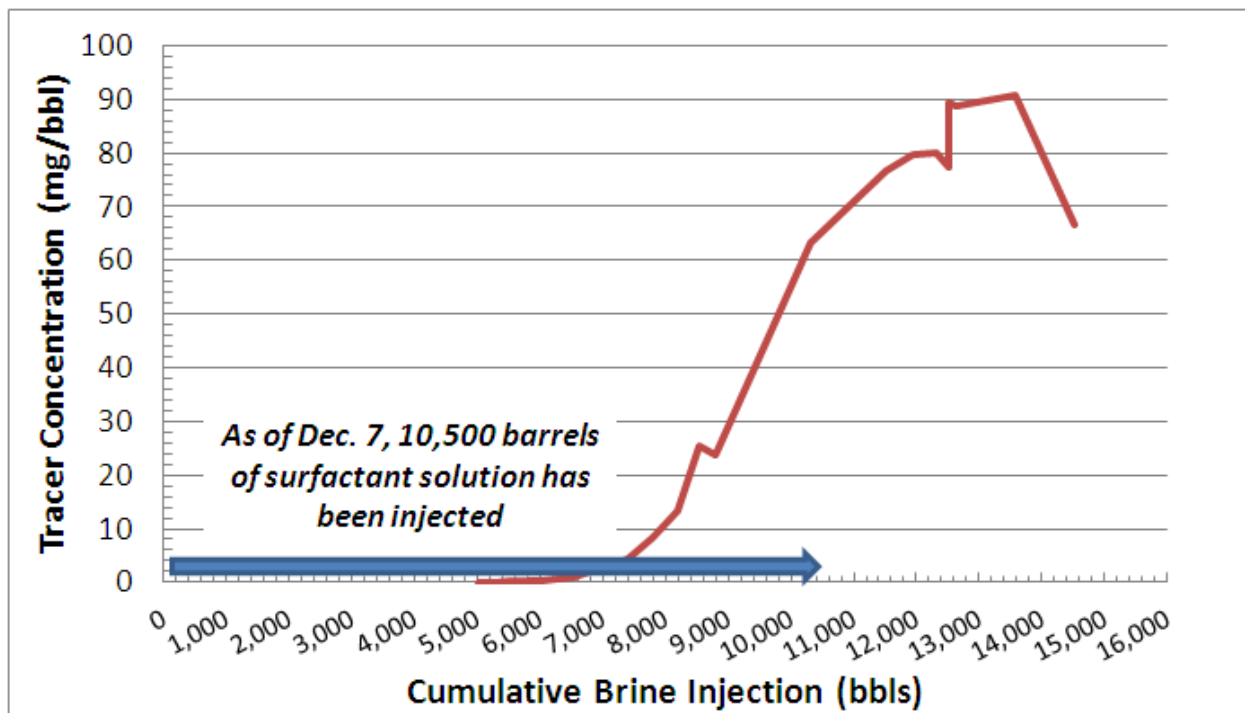


Fig. 1.33. Delivery of dual surfactant mixture on site



Fig. 1.34. Example of production well sample



1.6.1 Summary SK Site

The SK Site pilot surfactant injection started September 17th, 2013 and concluded March 13th, 2014. A total of 7,000 gallons of solution was injected. A commercial blender prepared the concentrated surfactant solution (53% active). The surfactant blend was then transported to the field in totes and offloaded to the field facility. The facility was a unique design that utilized a commercial bladder with 3,000 gallons of storage capacity. As the surfactant solution was drawn down, the bladder collapses effectively limiting headspace and preventing evaporative losses. A metering pump injected the surfactant solution directly into the high pressure injection line at the well. A static mixer ensured adequate mixing of the surfactant solution with the injection brine. A flow meter at the well head controlled the injection rate of the metering pump to ensure we injected 0.5%-wt. surfactant solution. The surveillance program consisted on collecting high concentration surfactant samples, samples of mixed solution and injection brine at the injection well head, and samples of produced oil and brine from the producing well. At this time, surfactant breakthrough has not been observed and the pilot monitoring would continue through October 2014. It is suspected that higher than expected absorption has caused a delay of surfactant breakthrough or has completely consumed the chemical slug.

Chapter 2. Developing Crude Oil Fingerprinting Tool for Reducing Uncertainty of Field Chemical EOR

2.1 Geochemical study of crude oil-composition analysis

2.1.1. Crude SARA Fraction analysis

2.1.1.1, Asphaltenes separation follows the Standard Method of Institute of Petroleum

- Add into a conical flask weigh 2.00 g of crude oil
- Add 20 mL of nearly boiling Ligroin (Sigma-Aldrich Cat# 333417-2L) into the flask
- Mix the oil and solvent (Ligroin) thoroughly and allow to stand in the closed flask in the dark for 24 hours
- Without agitation, decant the liquid through an 11-cm medium-texture filter paper (Whatman No. 40)
- Transfer the residue in the flask as complete as possible to the filter paper with successive quantities of hot ligroin, using a glass rod to ensure thorough extraction of the residue with the solvent. Give the flask a final rinse with hot ligroin and pour the rinsings through the filter paper
- Place the filter paper and its contents in a Soxhlet extraction system, and reflux it with ligroin for about 60 minutes.
- Use benzene (Sigma-Aldrich Cat# 270709-2L) to flux the filter paper and its contents for additional 30 minutes
- Weight a glass evaporating dish to nearest 0.20 mg by tare against a similar dish
- Transfer the extract from the Soxhlet to the evaporation glass dish
- Use benzene to wash the Soxhlet system twice, and pour the benzene to the evaporating glass dish

- Dry the dish containing the extract in chemical hood and weight the dish again
- Calculate asphaltenes content as a percentage by weight of the original crude oil
- Dissolve the asphaltenes by toluene and analyzed by GCFID/GCMS

2.1.1.2. Deasphalted crude oil that was dissolved by ligroin (see method for separating asphaltenes described in 1-1 section) was used to fraction saturates (straight-chain hydrocarbons), aromatics (aromatic hydrocarbons) and resins. An open column chromatographic method was used for the separation.

- Add equal quantities of Silica and Alumina into a Peroxide-Cured Reinforced Silicone Tubing (Inter Diameter = 1", Cole-Parmer Cat# S-95623-10).
- Use a Berea sandstone plug (500MD) to block one end of the tubing
- Add 10g of Silica Gel (Dynamic Adsorbents Inc. Cat# 04530-05) to the tubing building up a silica layer on the top of the sandstone plug.
- Add 10g of Alumina Basic Act. 1 (Dynamic Adsorbents Inc. Cat# 02078-05) building up an alumina layer on the top of the silica layer
- Pour deasphalted crude into the tubing, and let it gravitate through alumina layer and silica layer
- Use hexane to elute saturates (straight-chain hydrocarbons) from the column (gravitating flow)
- Subsequently use benzene to elute the aromatic hydrocarbons (gravitating flow)
- Finally use methanol to elute the resins from the column (gravitating flow)
- Three fractions collected from the silica-alumina column were quantitatively analyzed by GCFID and GCMS instruments

- Calculate their percentage by weight of the original crude oil

Saturates, Aromatics, Resins and Asphaltenes (SASA) fractions of crude oils from four oil fields (W, SK, M and H Site) are determined (Table 2.1).

Table 2.1. SARA analysis of four crudes

	W Site	SK site	M Site	H Site
Saturates	50.4%	57.2%	52.5%	55.0%
Aromatics	10.0%	40.5%	47.0%	4.9%
Resins	39.6%	2.3%	0.4%	40.1%
Asphaltenes	2.6%	1.8%	1.5%	6.0%

Crude oil fractions could have impact on the interfacial tensions (IFTs), which is the most critical parameter of EOR. The interstitial water may be one of the major factors controlling the behavior of chemical solutions in the sandstones. Some papers indicate chemical reactions between surfactant solution, resins fraction of crude oil and alkaline solutions of the interstitial water of sandstones could produce *in situ* surfactants. Further analyses indicate that for different crude oils, saturates could contain various quantities of branched-chain paraffins and straight-chain paraffins, aromatics could contain various amounts of paraffins, aromatics and pathalic acid, resins could contain various amounts of alcohols and petroleum acids (See Figures 2.1, 2.2 and 2.3 in the followings). More studies are need to determine the detailed compositions.

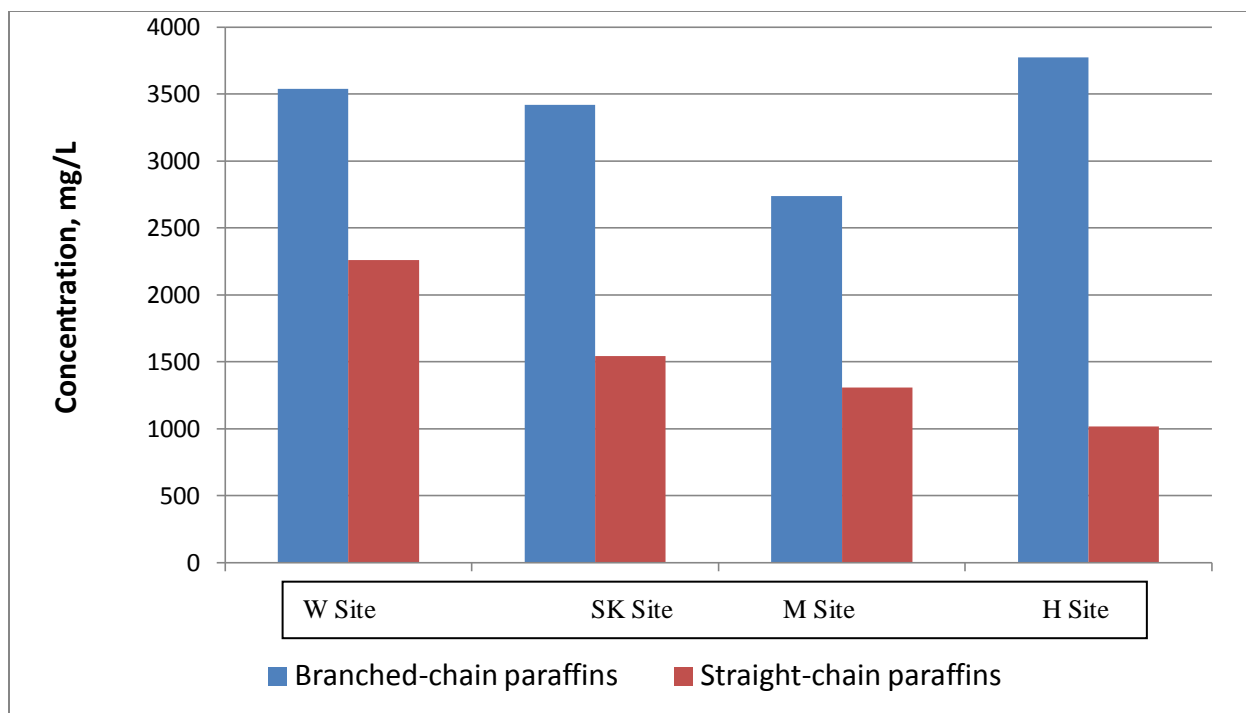


Figure 2.1. Chromatography data show composition of saturates

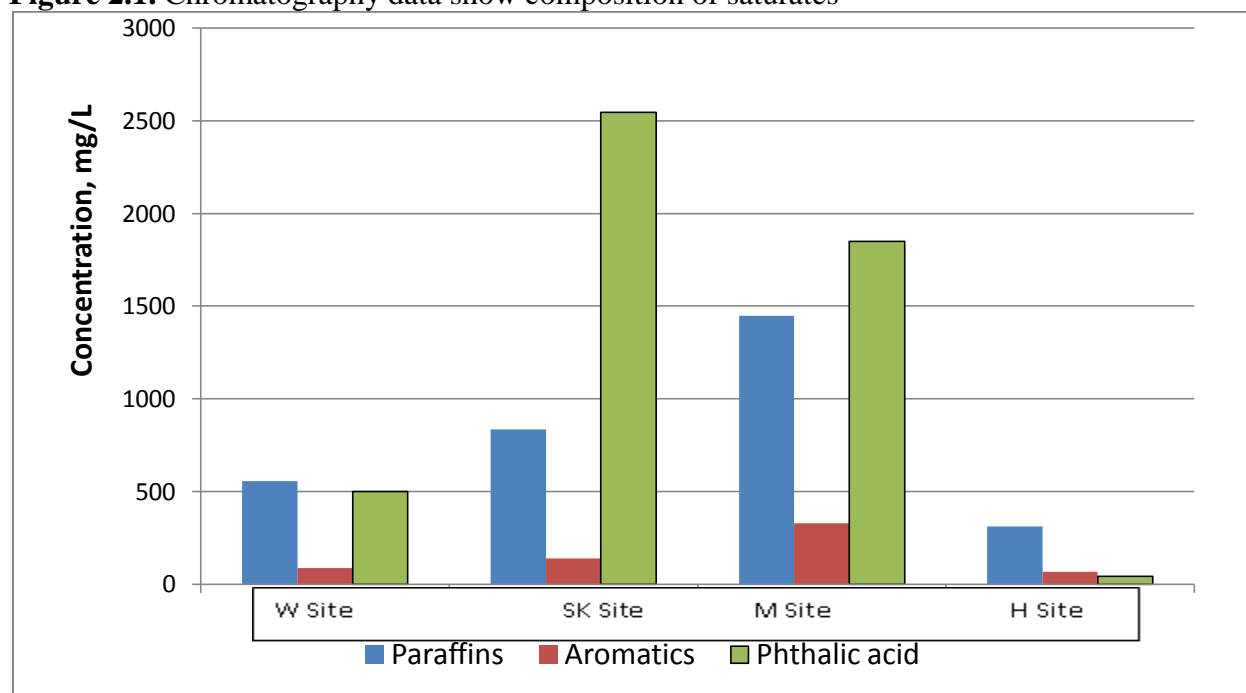


Figure 2.2. Chromatography data show composition of aromatics

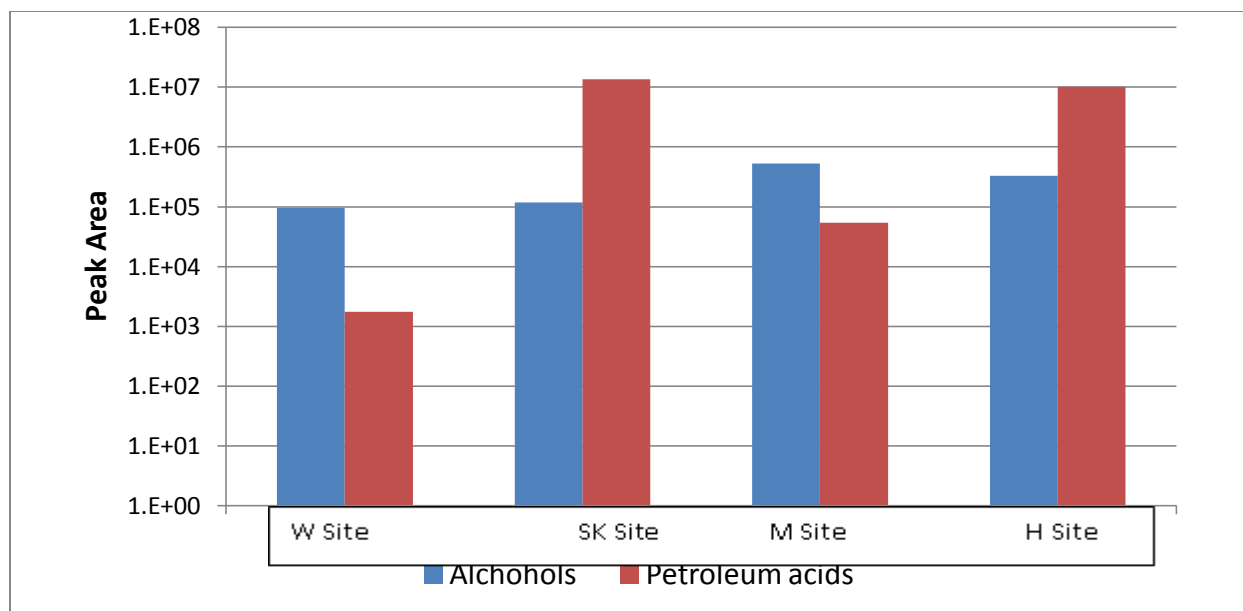


Figure 2.3. Chromatography data show composition of resins

2.1.2. Fingerprints analysis

Asphaltenes are capable to occlude species (e.g., alkanes) inside the skeleton, keeping them from biodegradation. These remnants of the “original oil” become fingerprints for studying crudes in correlation with their genesis. It has been extremely difficult to determine compositions of asphaltenes by using a normal method due to noise on chromatogram (see figure on right).

Chemical treatment could reduce noise greatly.

Pyrolysis of asphaltenes could release these occluded species and was considered to be an useful tool to study the correlation of crudes. However, a commercial pyroprobe is very expensive (see Table 2.2).

Table 2.2. Price range for the common CDS pyroprobes

CDS Pyroprobe	Cost range, \$	
CDS 5200	28,000-42,000	
CDS 5000	21,000-25,000	
CDS 4000	12,000-15,000	
CDS 2000 (used)	8,000-9,000	This product is not supported by CDS

Chemical treatment can also free the occluded species from asphaltene molecules. The hydrocarbons obtained after oxidation of asphaltenes are remnants of the “original oil” occluded by the asphaltene molecule. According to Z. Liao and A. Geng (*Organic Geochemistry*, 2002), a chemical method was developed for the fingerprints analysis of asphaltenes.

- Before chromatography analysis, asphaltene was treated chemically by mixture of $\text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$
- Take a 500 mg of asphaltene into a 250-mL flat bottom flask
- Add 50 mL benzene into the flask to dissolve asphaltene
- Mix 1 mL of 30% H_2O_2 and 10 mL of glacial acetic acid (CH_3COOH) in a 50 mL beaker
- Transfer the oxidative solution into the flask containing asphaltene
- Keep the mixture fully agitated at room temperature for 12 hours
- Use a separating funnel to separate the benzene from glacial acetic acid
- The benzene solvent was concentrated in a Turbo Vap-II evaporator to 1.0 mL for chromatography analysis

The chromatography data are presented in Figure 2.4

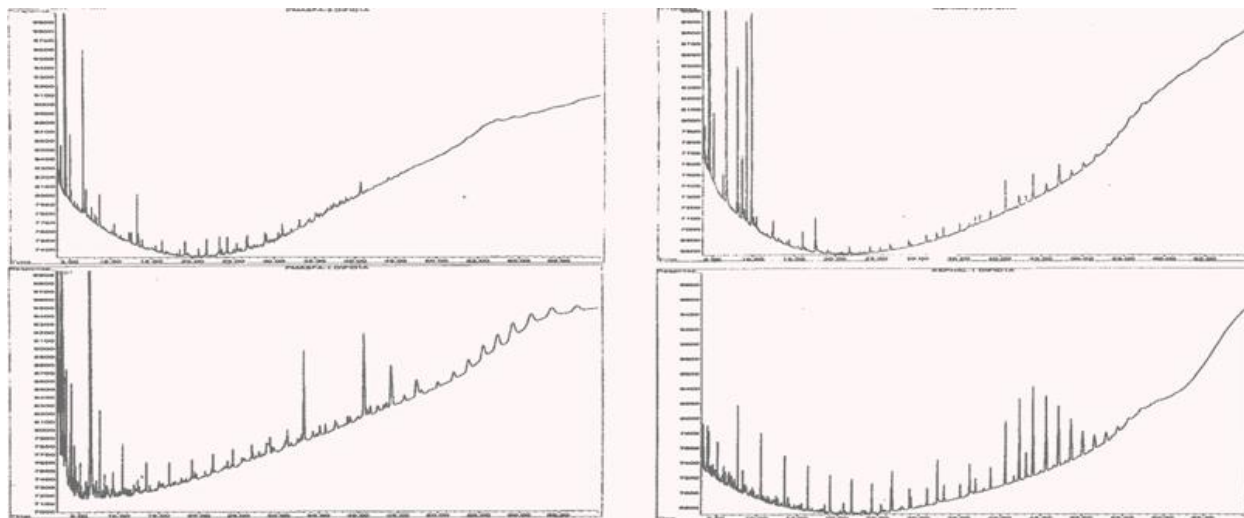


Figure 2.4. Analysis of asphaltenes from W Site and H Site crude oils

Left: Asphaltenes from W Site crude analyzed at 400 °C (upper chromatogram), and chemically treated and analyzed at 250 °C (lower chromatogram)

Right: Asphaltenes from H Site crude analyzed at 400 °C (upper chromatogram), and chemically treated and analyzed at 250 °C (lower chromatogram)

The lab data show asphaltenes from different crude oils contain various components, which indicate these crudes may come from different original materials and reservoir conditions.

2.2. Petrophysical study of reservoir sandstones

2.2.1. NMR study of sandstone

Fluvial-Dominated Deltaic Sandstone (FDD) reservoirs are the most important light-oil reservoirs in the state of Oklahoma. Geologically, FDD reservoirs are of Pennsylvanian-age. Pennsylvanian contains five series. Desmoines series of the Middle Pennsylvanian represents the most important oil-bearing sandstone formations, which contribute crude production greater than 50% of recovery from the whole Pennsylvanian system. In this study, the main target formations would be among these oil-bearing sandstone formations. They are Bartlesville, Red Fork, Skinner-Prue, Cleveland and Peru sandstone formations.

A total of 23 core plugs were collected from the Oklahoma Geological Survey's Oklahoma Petroleum Information Center (OGS-OPIC). These core plugs represent five major oil-bearing sandstone formations in Oklahoma. Detailed information of these core plugs are described in Table 2.3.

Table 2.3. List of Core Plugs Collected From GS-OPIC

OGS-OPIC File #	Drilling Operator	Well Name	Sandstone Formation	Original Depth (Feet)	Plug #
937	Jenkins & Basin	Holzer	Cleveland	3782	1
937	Jenkins & Basin	Holzer	Cleveland	3803	2
937	Jenkins & Basin	Holzer	Cleveland	3812	3
937	Jenkins & Basin	Holzer	Cleveland	3815	4
937	Jenkins & Basin	Holzer	Cleveland	3823	5
272	Gulf	Deep Fork Un	Skinner-Prue	2447	6
272	Gulf	Deep Fork Un	Skinner-Prue	2454	7
272	Gulf	Deep Fork Un	Skinner-Prue	2456	8
272	Gulf	Deep Fork Un	Skinner-Prue	2467	9
2325	Lear Petr	Byfield	Red Fork	5699	10
2325	Lear Petr	Byfield	Red Fork	5720	11
1930	Ong	Trindle	Bartlesville	6597	12

1930	Ong	Trindle	Bartlesville	6603	13
1930	Ong	Trindle	Bartlesville	6606	14
1930	Ong	Trindle	Bartlesville	6609	15
2404	Ratiff	Penick	Peru	7947	16
2404	Ratiff	Penick	Peru	7954	17
2404	Ratiff	Penick	Peru	7956	18
2404	Ratiff	Penick	Peru	7962	19
4658	Continental & Res Corp	Grace	Red Fork	4969	20
4658	Continental & Res Corp	Grace	Red Fork	4971	21
4658	Continental & Res Corp	Grace	Red Fork	4973	22
4658	Continental & Res Corp	Grace	Red Fork	4975	23

It is planned to use these core plugs for mineralogical and petrophysical study, such as sandstones compositions, porous texture by using different instruments, including X-Ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR) spectroscopy and Nuclear Magnetic Resonance spectroscopy. We investigated Berea sandstone using NMR method. The NMR T_2 spectrum indicate that the pore size of the column filled with crushed Berea sandstone have different T_2 relaxation times for water, crude oil and surfactant. The NMR T_2 relaxation time of core with crude oil-saturated differed from that of core with water-saturated may suggest NMR would be a tool for the evaluation of pore geometry distribution and oil saturation degree of reservoir rock. Unfortunately, we can't continue petrophysical study of core plugs collected

from OGS-OPIC.

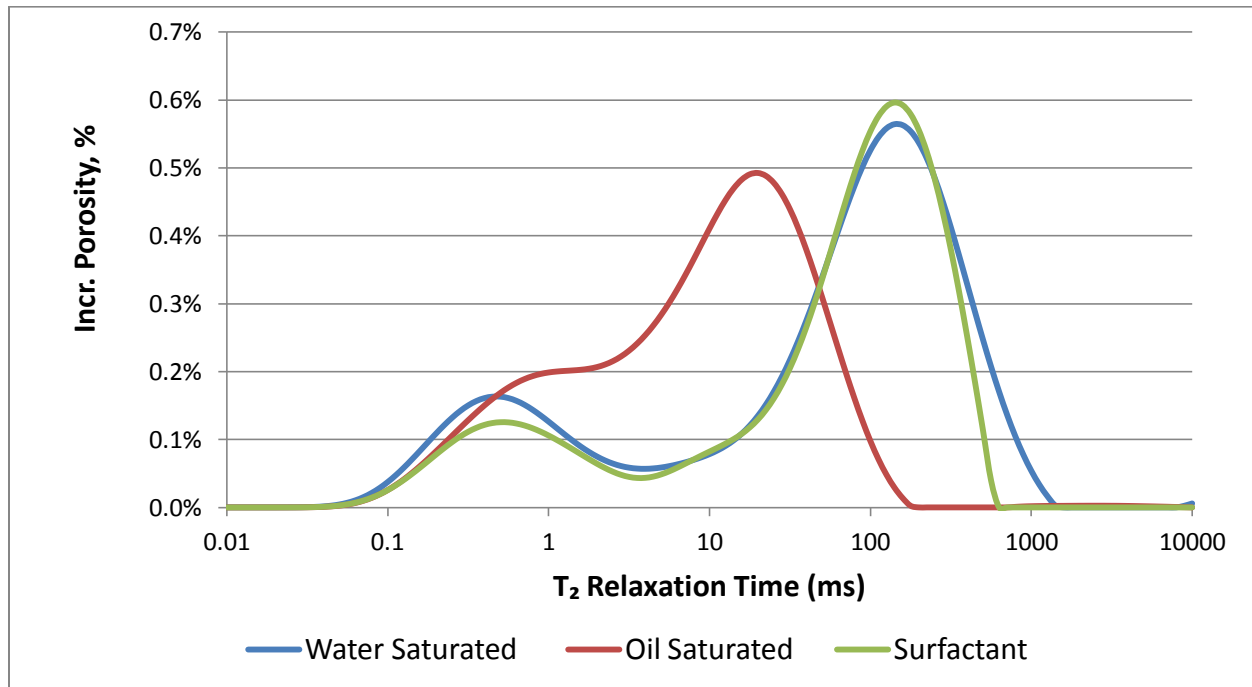


Figure 2.5. NMR data of 500MD Berea sandstone column saturated with oil, water and surfactant.

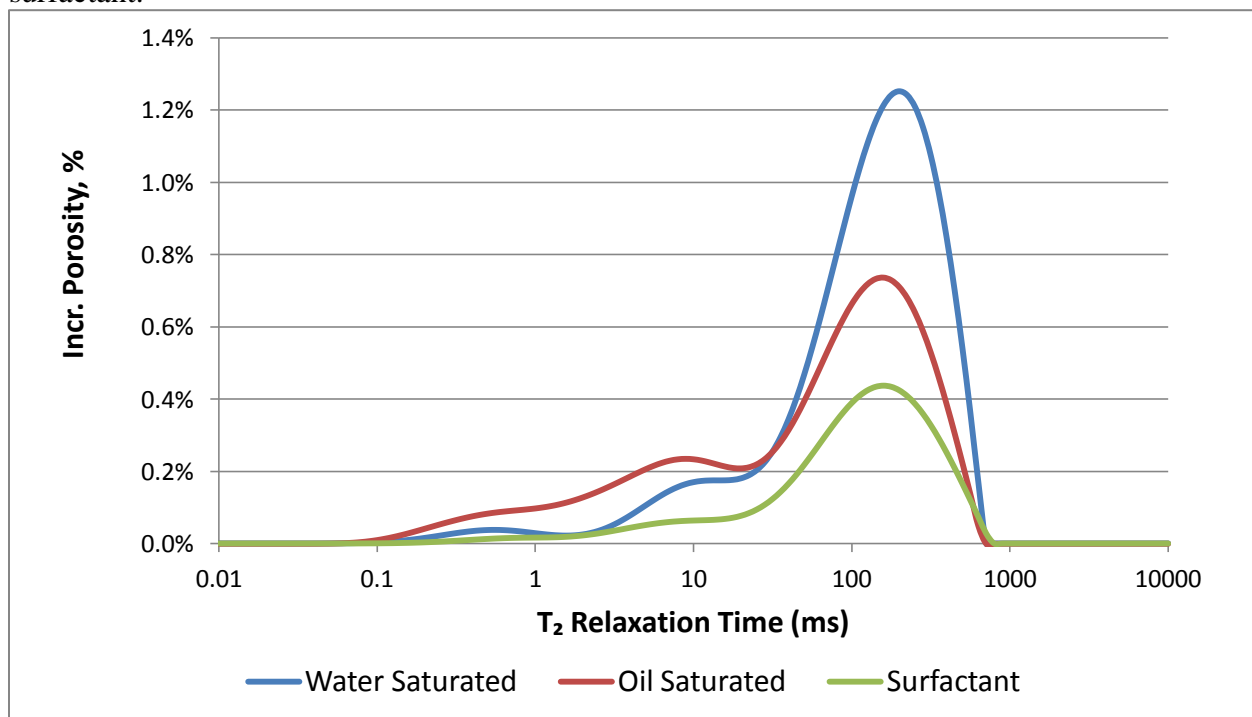


Figure 2.6. NMR data of 50MD Berea sandstone column saturated with oil, water and surfactant.

2.2.2. Geochemical study of reservoir quality

2.2.2.1. Crude SARA Fractionation

Asphaltenes separation following IP Standard Method

Asphaltene residue was dissolved with benzene for GCMS analysis.

Deasphalted crude

Open column chromatographic method by using silica/alumina adsorbents and subsequent elution with hexane, benzene and methanol for saturates, aromatics and resins separation. The three fractionations were analyzed by GCFID and GCMS.

SASA fractions in four crude oils

Table 2.4.

	W Site	SK Site	M Site	H Site
Saturates	50.4%	57.2%	52.5%	55.0%
Aromatics	10.0%	40.5%	47.0%	4.9%
Resins	39.6%	2.3%	0.4%	40.1%
Asphaltenes	2.6%	1.8%	1.5%	6.0%

Chapter 3. Numerical Simulation Efforts

3.1. Numerical Interpretation of Single Well Chemical Tracer Test (SWCTT)

3.1.1. Introduction

SWCTT is a well-established technique in determining residual oil saturation (S_{or}). This method has its advantage over logging because the injected tracer directly contacts with residual oil, and the detected area is much bigger. From the production tracer profiles, the average S_{or} can be calculated by the retardation of ester over alcohol and given partitioning coefficient. However, the approximate S_{or} depends on the validity of several assumptions: 1) Hydrolysis reaction occurs only during shut-in period (no flow), so that tracer B (Material Balance Tracer) and unreacted tracer A (Partitioning Tracer) are exactly together before back flow begins; 2) S_{or} is uniform throughout the interested formation, and 3) The mixing associated with flow through the porous medium effects partitioning and material balance tracer in the same way.

Due to the complex field test processes and geological uncertainties, numerical simulation method was used to interpret the field test results. Popular reservoir simulator CMG STARS was selected to model the SWCTT because of its good computational capabilities and chemical reaction features. Permeability, porosity, payzone thickness and partitioning coefficient were treated as input data. Partitioning coefficient was measured in the lab under reservoir temperature and formation water salinity. The number of layers, S_{or} , dispersivity coefficient, flow fraction in each layer, and reaction rate were used as the matching parameters.

Three SWCTT including SF #56, H and WP were numerically interpreted. In dealing with the tracer material balance from field test results, the concentrations of Ethyl Formate, Methanol and n-Propanol were kept constant and the flow rates of primary tracer and pusher injection were adjusted by multiplying the percentage of recovery.

3.1.2 SF56 Site

In the SF field, the Bartlesville formation is characterized by moderate permeability ranging from 50 to 100 mD , porosity of 15-19%, pay thickness of 20 ft and light crude of ~4 cP oil at reservoir temperature.

The numerical simulation results of pre- and post SWCTT at SF well #56 are shown in Figures 3.1 and Figure 3.2, and the matching parameter are summarized in Table 3.1. Numerical simulation results indicate the residual oil saturation was reduced from 0.49 and 0.22 to both 0.15 in each layer.

3.1.3 H Site

In the H site, the Deese formation is characterized by low permeability of 25 mD, porosity of 15-19%, pay thickness of 9 ft and higher oil viscosity of 25 cP.

The numerical simulation results of pre- and post SWCTT at H Site are shown in Figure 3.3 and Figure 3.4, and the matching parameter are summarized in Table 3.2.

3.1.4 W Site

W Reservoir, which is located in the state of Oklahoma, USA, as shown in Figure 3.5, is characterized by permeability ranging from 500 to 1000 mD, porosity of 20%, pay thickness of 12 ft and light crude of ~3.5 cP oil at reservoir temperature of 52 °C.

Figures 3.6 through 3.8 present the matching profiles of pre-SWCTT with different Sor. With Sor of 0.20, 0.16 and 0.11, all results are well matched with reaction rate of $1.40 \times 10^{-4} \text{ s}^{-1}$, $1.20 \times 10^{-4} \text{ s}^{-1}$, and $7.9 \times 10^{-5} \text{ s}^{-1}$. Since reaction rate of $7.9 \times 10^{-5} \text{ s}^{-1}$ is the one most close to the reaction rate measured at lab, Sor of 0.11 is the best matching results for pre-SWCTT of W Site. The matching profile of material balance tracer Methanol in pre-SWCTT is shown in Figure 3.9.

Figure 3.10 shows the matching results for post-SWCTT with Sor of 3%, indicating good surfactant flooding efficiency. And Figure 3.11 shows the matching profile of material balance tracer Methanol in post-SWCTT. Table 3.3 shows all matching parameters.

3.2. Interwell tracer test (IWTT) at SK Site

3 kg of conservative tracer 2-FBA was injected in 30 min into Well PA9. And its breakthrough time was 35 days in Well PA4, which is 422 ft far from PA9. The average injection rate of Well PA9 was 138 bbls/day, and the production rate of Well A4 was constant at 150 bbls/day. The plot of tracer concentration versus time is shown in Figure 3.12 and followed by analytical calculation of water flow fraction of injected water and swept volume.

Method of moments was used to estimate the injected water flow fraction and swept volume.

Constant a is evaluated at the point of data extrapolation from the equation

$$C = \frac{C_0}{1 + a t} \quad (1)$$

The first temporal moment is then estimated as

$$M_1 = \frac{\int_0^\infty t C dt}{\int_0^\infty C dt} \quad (2)$$

To estimate the amount of 2-FBA produced at Well PA4,

$$M_1 = \frac{Q_p}{Q_i} M_1 \quad (3)$$

Water flow fraction from Well PA9 to Well PA4 is

$$f_w = \frac{M_1}{M_1} \quad (4)$$

The net swept volume is then given by

$$V_s = \frac{Q_p}{f_w} M_1 \quad (5)$$

A quadrant pattern was selected to match the tracer production history in Well PA4, as shown in Figure 3.13. The injection rate was adjusted to 46.5 bbls/day according to the flow fraction. And

the production rate of Well PA4 was set same as the injection rate to maintain material balance in the simulation. Matching parameters include permeability, formation thickness and dispersivities.

The fitting parameters are summarized in Table 3.4, and the matched result is presented in Figure 3.14.

3.3. Simulation of Column Test

3.3.1. Converting Surfactant Scan to Salinity Scan

To develop optimum surfactant formulation for high salinity reservoirs, the strategy is to do phase behavior and IFT test by varying the ratio of surfactants with different hydrophilic-lipophilic properties. Hydrophilic Lipophilic Difference (HLD) equation correlates the important variables in the achievement of the low IFT in a W/O/S/electrolyte system, and is shown in Eq.6.

(6)

where, S = salinity, g of NaCl per 100ml brine.

ACN = number of carbon atoms in an alkane

K = slope of the logarithm of optimum salinity as a function of CAN

$f(A)$ = function of alcohol type and concentration

= characteristic parameter of surfactant

= temperature coefficient of optimum salinity expressed in units of $\ln S$ per $^{\circ}C$

T = temperature, $^{\circ}C$

Characteristic curvature (Cc) from HLD equation is a new parameter to quantitatively describe the surfactant hydrophilic-lipophilic property. The HLD approaches zero when the surfactant mixture approaches optimum.

Hand's rule is the phase behavior model implemented in UTCHEM to calculate the phase saturation and composition at different salinity by treating surfactant as a pseudo component. There are five Hand's rule parameters in UTCHEM to calculate the phase behavior, which are HBNC70, HBNC71, HBNC72, CSEL7 and CSEU7. The concepts of these parameters are summarized in Table 3.5.

Table 3.6 summarizes the HLD parameters of surfactant AF-10-41S and Steol Cs 460, which are candidate surfactant for War Party. Figure 3.15 shows the IFT behavior of Steol Cs 460 scan with AF-10-41S as the main surfactant at the W Site formation salinity and temperature, indicating the system with AF-10-41S of 0.1 wt% and Steol Cs 460 of 0.2 wt% is the optimum system. And Table 7 shows the calculation of HLD of Steol Cs 460 scan, where the HLD of the system with AF-10-41S of 0.1 wt% and Steol Cs 460 of 0.16 wt% close to zero. This report adjusted the ϕ of the mixture from 0.0075 to 0.006 to let the calculated HLD be consistent with the IFT measurement.

In order to express the phase behavior and IFT at different surfactant ratio by Hand's rule, this report defines "optimum Cc" expressing the optimum surfactant mixture characteristic at the reservoir salinity, and convert the Cc value of surfactant mixture to pseudo-salinity by keeping the HLD unchanging. The optimum Cc of surfactant mixture AF-10-41S and Steol Cs 460 is -2.06 at W Site formation condition. Table 8 shows the converted pseudo-salinity scan results and Figure 3.16 presents the IFT behavior of pseudo-salinity scan. Hand's rule parameters are then obtained by matching the equilibrium IFT of pseudo-salinity scan. Figure 3.17 shows the matched results and Table 3.5 summarizes the matched Hand's rule parameters.

3.3.2. History Matching of Sand Pack Flooding

Sand pack was firstly saturated with oil, and was water flooded 3PV, followed by 1 PV of 0.75 wt% of optimum surfactant formulation, and then followed by 3 PV of water flooding. Figure 3.18 plots the cumulative oil recovery during surfactant flooding and post chemical water flooding process for Berea sand and Ottawa sand, respectively. The porosities of Berea and Ottawa sand pack are 0.407 and 0.381, and water flooding Sor for Berea and Ottawa sand pack are 0.284 and 0.240.

UTCHEM uses Eq. 7 to calculate the residual oil saturation vs. capillary number,

$$\text{—————} \quad (7)$$

where τ is trapping parameter as a matching parameter. This report uses typical values of trapping parameters from sandstone, as shown in Table 3.9.

Relative permeability curves and adsorption were used as matching parameters. In UTCHEM, relative permeability curves are expressing by Corey's model, as shown in Eqs. 8 and 9,

$$\text{for } l = w, o, \text{ or } m \quad (8)$$

where the phase normalized saturation are given by

$$\text{—————} \quad \text{for } l = w, o, \text{ or } m \quad (9)$$

The matched relative permeability curves parameters are summarized in Table 10, and the matched relative permeability curves are plotted in Figures 3.19 to 3.22. The matched adsorption for Berea and Ottawa sand pack are 5.4 mg/g and 2.5 mg/g. And the matched results of surfactant flooding cumulative oil recovery curves for Berea and Ottawa sand pack are shown at Figures 3.23 and 3.24.

Table 3.1. – Matching parameters of SWCTT simulation for SF #56 Site

Matching Parameter	Pre		Post	
	1 st Layer	2 nd Layer	1 st Layer	2 nd Layer
Tracer injection fraction	0.05	0.95	0.09	0.91
Pusher injection fraction	0.08	0.92	0.14	0.86
Back flow fraction	0.23	0.77	0.39	0.61
Reaction rate constant, s ⁻¹	4.0e-5	4.0e-5	2.4e-5	3.5e-5
Dispersion coefficient (EtF)	0.0008	0.0065	0.001	0.04
Dispersion coefficient (EOH)	0	0.003	0	0.04
Residual Oil Saturation	0.49	0.22	0.15	0.15

Table 3.2. – Matching parameters of SWCTT simulation for H Site

Matching Parameter	Pre		Post	
	1st Layer	2nd Layer	1st Layer	2nd Layer
Tracer injection fraction	0.45	0.55	0.39	0.61
Pusher injection fraction	0.41	0.59	0.69	0.31
Back flow fraction	0.63	0.37	0.82	0.18
Reaction rate constant, s-1	7.0e-5	7.0e-5	4.5e-5	4.5e-5
Dispersion coefficient (EtF)	0.05	0.02	0.01	0.01
Dispersion coefficient (EOH)	0.04	0.03	0.012	0.015
Residual Oil Saturation	0.20	0.12	0.03	0.03

Table 3.3. – Matching parameters of SWCTT simulation for W Site

Matching Parameter	Pre	Post
	Simulation	Simulation
Porosity	0.3	0.27
Reaction Rate (s-1)	9.50E-05	6.60E-05
Residual Oil Saturation	0.11	0.03
Dispersion coefficient (EtF)	0.009	0.013
Dispersion coefficient (EOH)	0.009	0.03
Tracer Injection Rate, m3/day	12.5	13
Pusher Injection Rate, m3/day	27.5	19
Production Rate, m3/day	24.65	22

Table 3.4. – Matching parameters of interwell tracer test for Well PA4 at SK site

Matching Parameter	Permeability, mD	Formation Thickness, ft	Longitude Dispersivity, ft	Transverse Dispersivity, ft
Value	393	4	8	0.4

Table 3.5. – Hand's rule parameters for W Site formulation

Hand's rule parameter	Value	Note
HBNC70	0.0700	Maximum height of binodal curve of added surfactant at zero salinity
HBNC71	0.0650	Maximum height of binodal curve of added surfactant at optimal salinity
HBNC72	0.0900	Maximum height of binodal curve of added surfactant at twice optimal salinity
CSEL7, meq/ml	4.1600	Lower effective salinity limit for type III phase region for added surfactant
CSEU7, meq/ml	5.0000	Upper effective salinity limit for type III phase region for added surfactant

Table 3.6. – HLD parameters of two surfactants

Surfactants	Cc Value	K value	Molecular Weight	
AF - 10-41s	-1.34	0.062	537.37	0.005
Steol Cs 460	-2.36	0.17	441	0.01

Table 3.7. – HLD calculation of Steol Cs 460 scan

AF 10-41S	Steol Cs 460	Cc-mix	K-mix	-mix	Ln(S)	EACN		HLD
0.1	0.14	-1.98305	0.116	0.0075	3.288402	9.2	27	0.035651
0.1	0.16	-2.0142	0.116	0.0075	3.288402	9.2	27	0.004507
0.1	0.18	-2.04059	0.116	0.0075	3.288402	9.2	27	-0.02188
0.1	0.2	-2.06323	0.116	0.0075	3.288402	9.2	27	-0.04453
0.1	0.22	-2.08288	0.116	0.0075	3.288402	9.2	27	-0.06418
0.1	0.24	-2.10009	0.116	0.0075	3.288402	9.2	27	-0.08139
0.1	0.26	-2.11529	0.116	0.0075	3.288402	9.2	27	-0.09659

Table 3.8. – HLD calculation of pseudo-salinity scan

AF 10-41S	Steol Cs 460	Cc-mix	K-mix	-mix	Ln(S)	EACN		HLD
0.1	0.2	-2.06323	0.1135	0.006	3.341585	9.2	27	0.072151
0.1	0.2	-2.06323	0.1135	0.006	3.310441	9.2	27	0.041007
0.1	0.2	-2.06323	0.1135	0.006	3.28405	9.2	27	0.014616
0.1	0.2	-2.06323	0.1135	0.006	3.261402	9.2	27	-0.00803
0.1	0.2	-2.06323	0.1135	0.006	3.241753	9.2	27	-0.02768
0.1	0.2	-2.06323	0.1135	0.006	3.224544	9.2	27	-0.04489
0.1	0.2	-2.06323	0.1135	0.006	3.209348	9.2	27	-0.06009

Table 3.9. – Parameters for capillary desaturation curve

Phase	Trapping Parameter
water	2000
oil	8000
microemulsion	1000

Table 3.10. – Matched parameters for relative permeability curves

Parameter	Value		Note
	Berea	Ottawa	
S1RW	0.33	0.4	Residual saturation of aqueous phase displaced by oil at low capillary number for entire reservoir
S2RW	0.30	0.26	Residual saturation of oleic phase displaced by water at low capillary number

			for entire reservoir
S3RW	0.3	0.40	Residual saturation of microemulsion phase displaced by water at low capillary number for entire reservoir
P1RW	0.3	0.20	End point relative permeability of water at low capillary number for entire reservoir
P2RW	0.95	0.95	End point relative permeability of oil at low capillary number for entire reservoir
P3RW	0.4	0.4	End point relative permeability of microemulsion at low capillary number for entire reservoir
E1W	12	12	Phase relative permeability exponent for aqueous phase at low capillary number for entire reservoir
E2W	1.5	1.5	Phase relative permeability exponent for oleic phase at low capillary number for entire reservoir
E3W	4	1.5	Phase relative permeability exponent for microemulsion phase at low capillary number for entire reservoir
S1RC	0	0	Residual saturation of aqueous phase displaced by oil at low capillary number for entire reservoir
S2RC	0	0	Residual saturation of oleic phase displaced by water at low capillary number for entire reservoir
E3RC	0	0	Residual saturation of microemulsion phase displaced by water at low capillary number for entire reservoir
P1RC	1	1	End point relative permeability of water at low capillary number for entire reservoir
P2RC	1	1	End point relative permeability of oil at low capillary number for entire reservoir
P3RC	1	1	End point relative permeability of microemulsion at low capillary number for entire reservoir
E1C	1	1	Phase relative permeability exponent for aqueous phase at low capillary number for entire reservoir
E2C	1	1	Phase relative permeability exponent for oleic phase at low capillary number for entire reservoir
E3C	1	1	Phase relative permeability exponent for microemulsion phase at low capillary number for entire reservoir

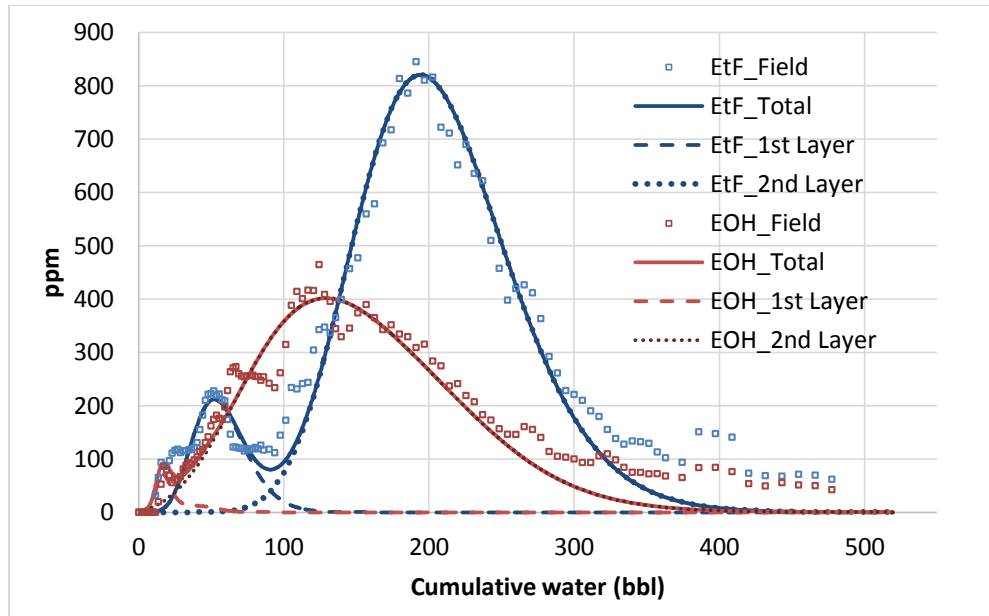


Figure 3.1. – Pre-SWCTT interpretation for SF #56

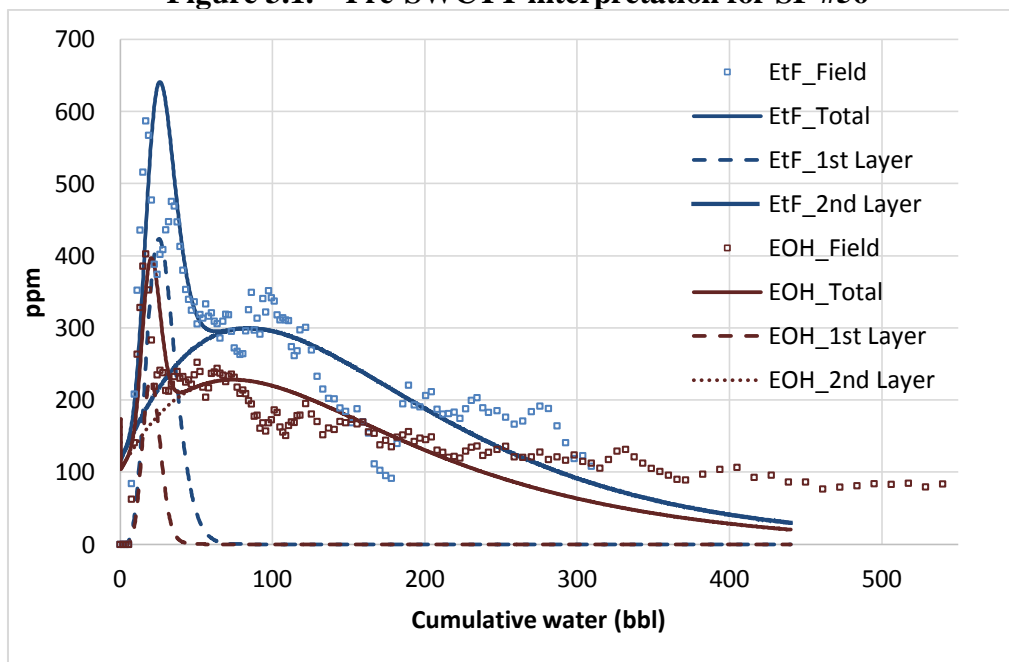


Figure 3.2. – Post-SWCTT interpretation for SF #56

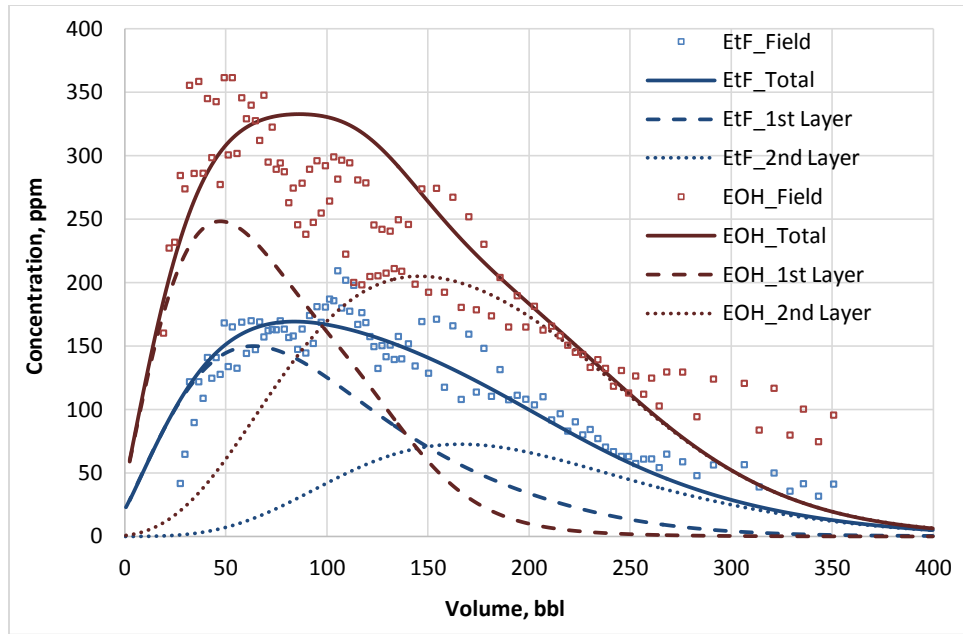


Figure 3.3. – Pre-SWCTT interpretation for H Site

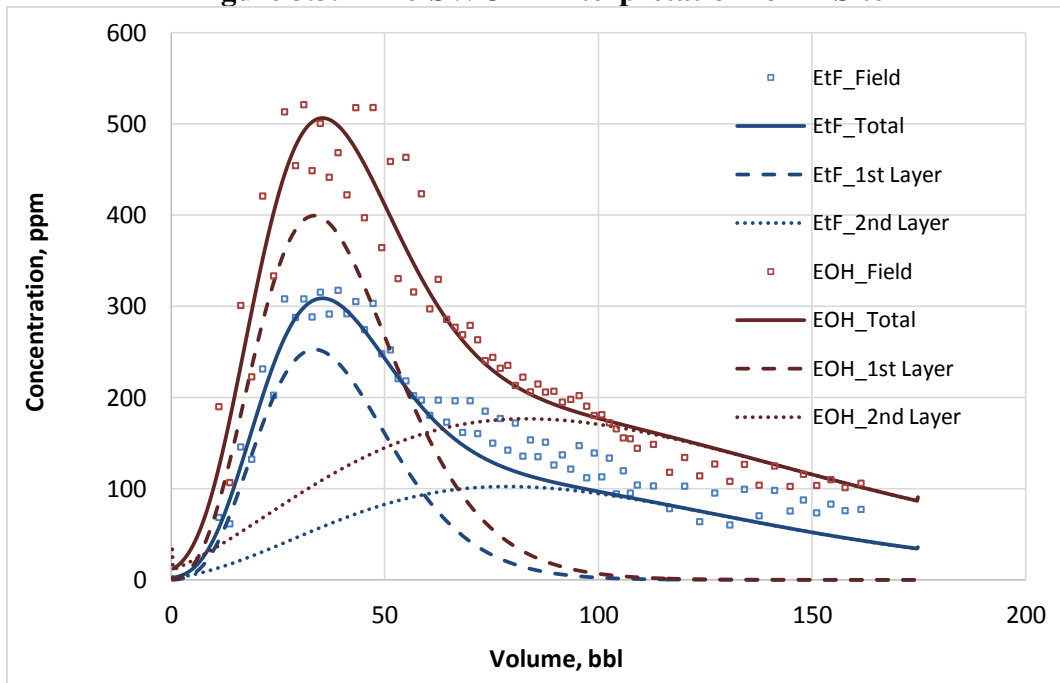


Figure 3.4. – Post-SWCTT interpretation for H Site

Oklahoma



Figure 3.5. – Location W Site Reservoir

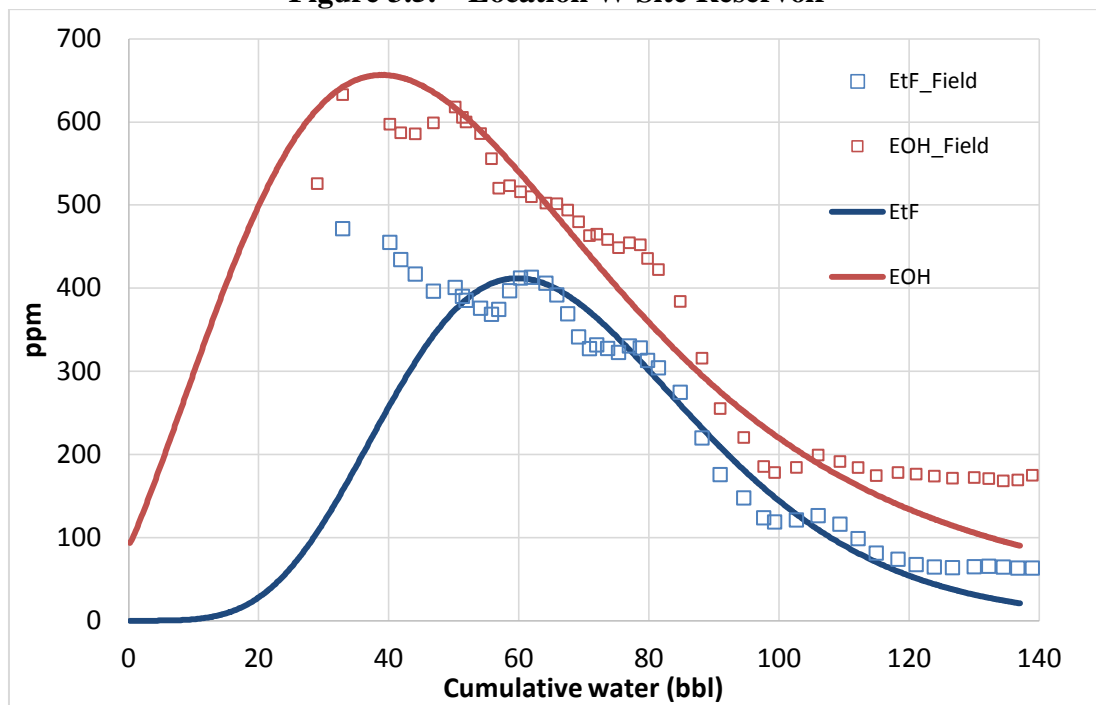


Figure 3.6. – Pre-SWCTT interpretation for W Site (Sor=0.20)

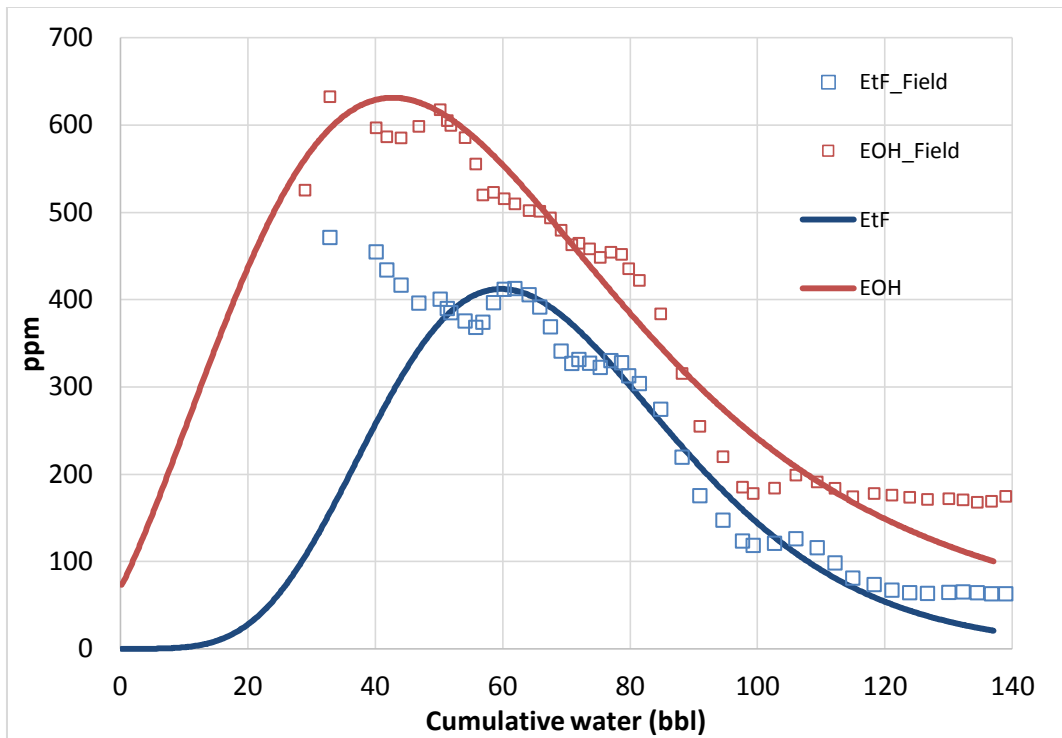


Figure 3.7. – Pre-SWCTT interpretation for W Site ($S_{or}=0.16$)

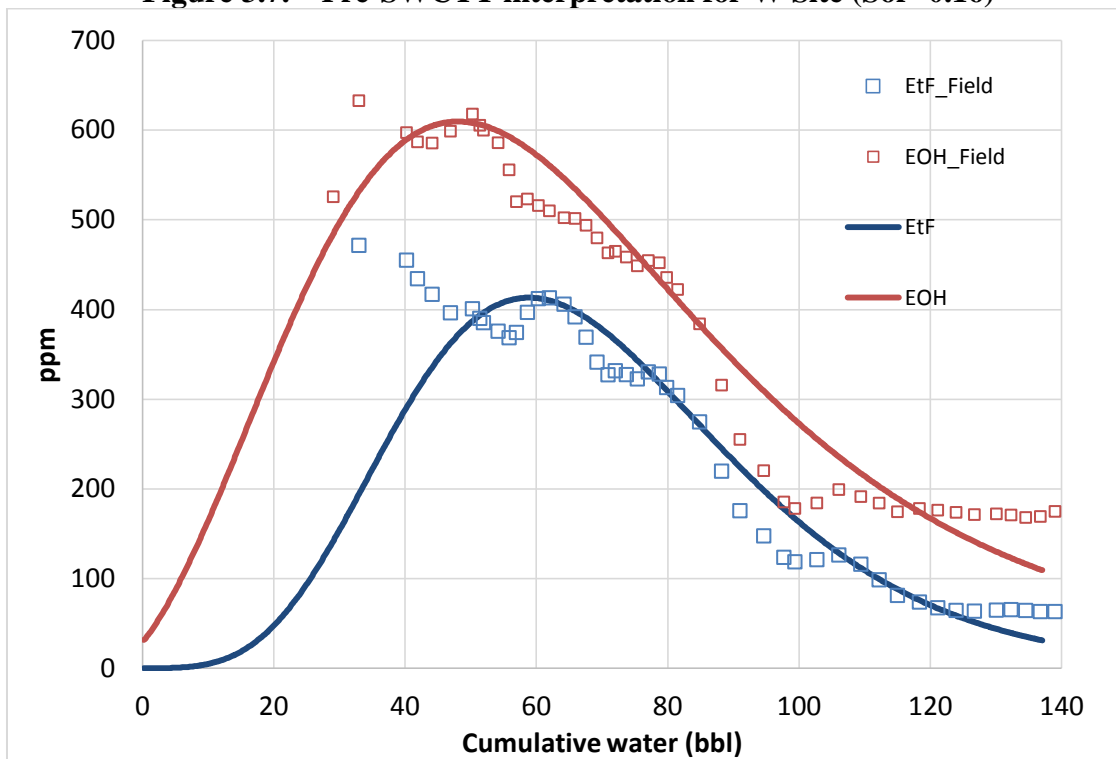


Figure 3.8. – Pre-SWCTT interpretation for W Site ($S_{or}=0.11$)

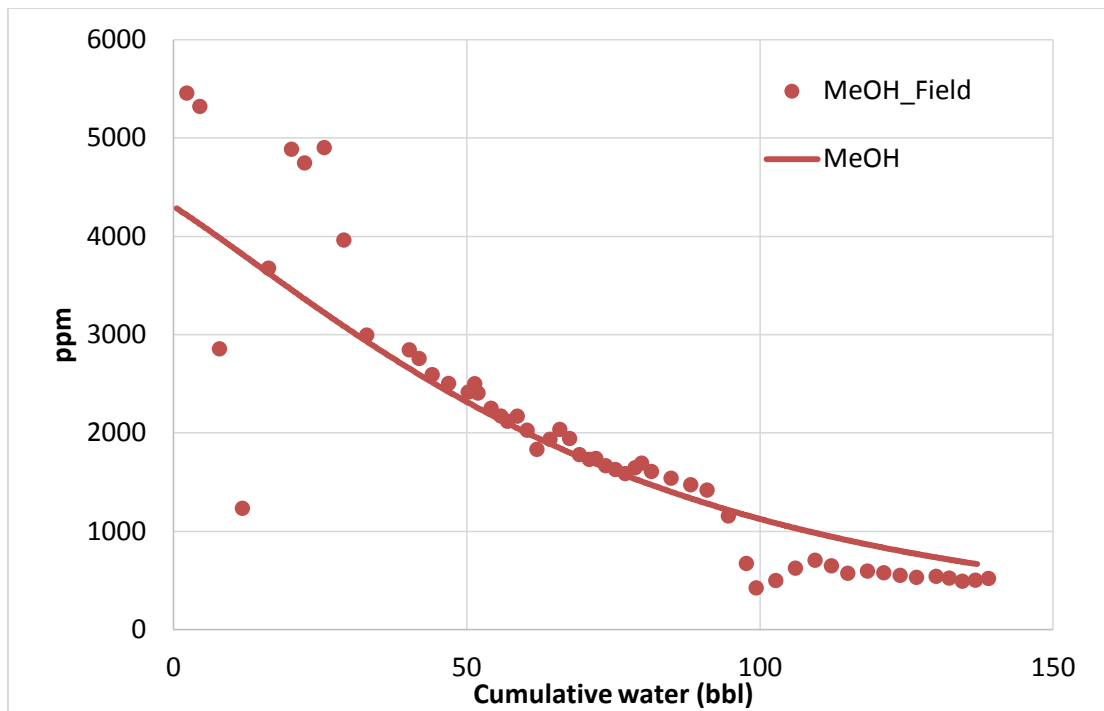


Figure 3.9. – Matching results of methanol concentration profile of Pre-SWCTT for W Site

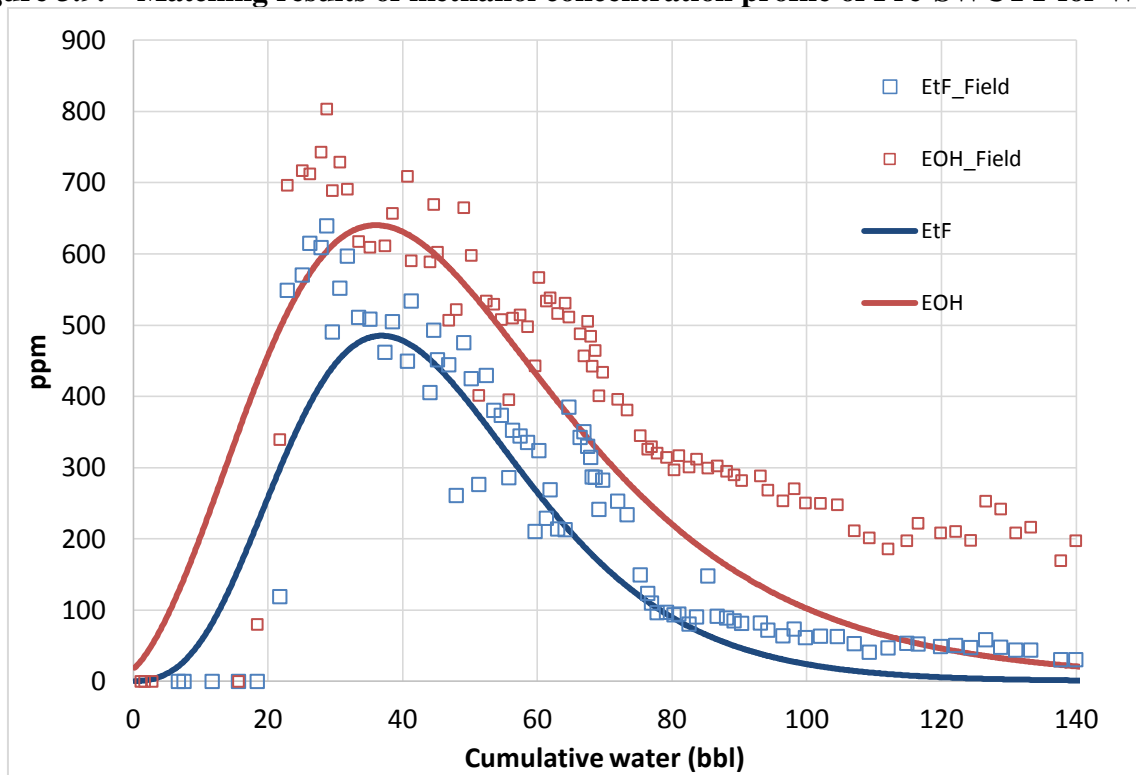


Figure 3.10. – Post-SWCTT interpretation for W Site

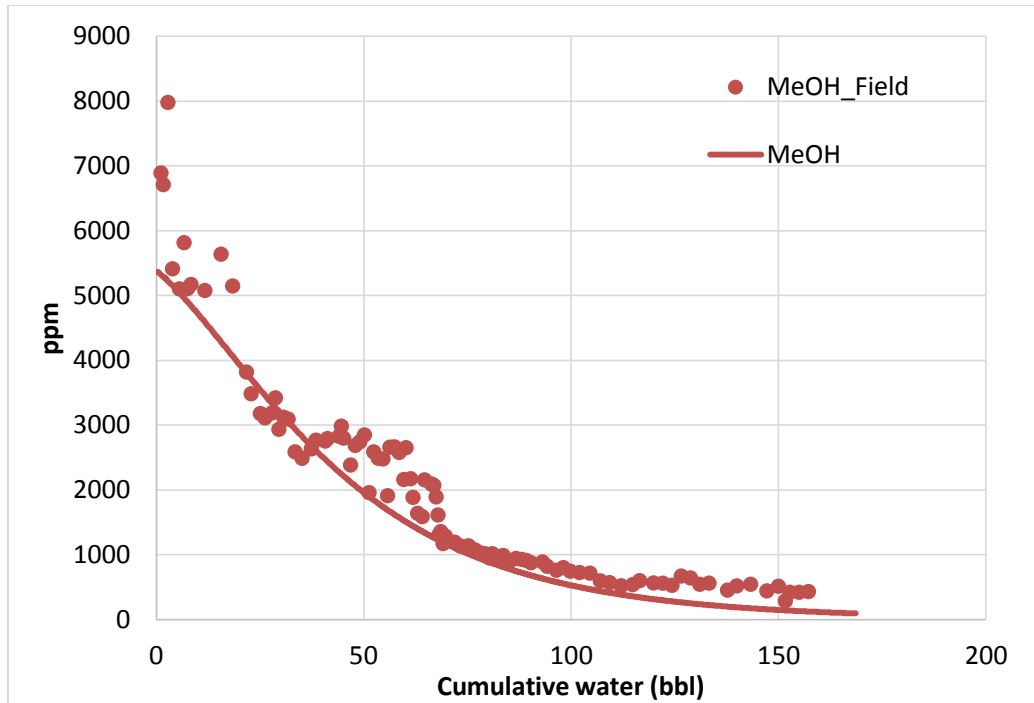


Figure 3.11. – Matching results of methanol concentration profile of Post-SWCTT for W Site

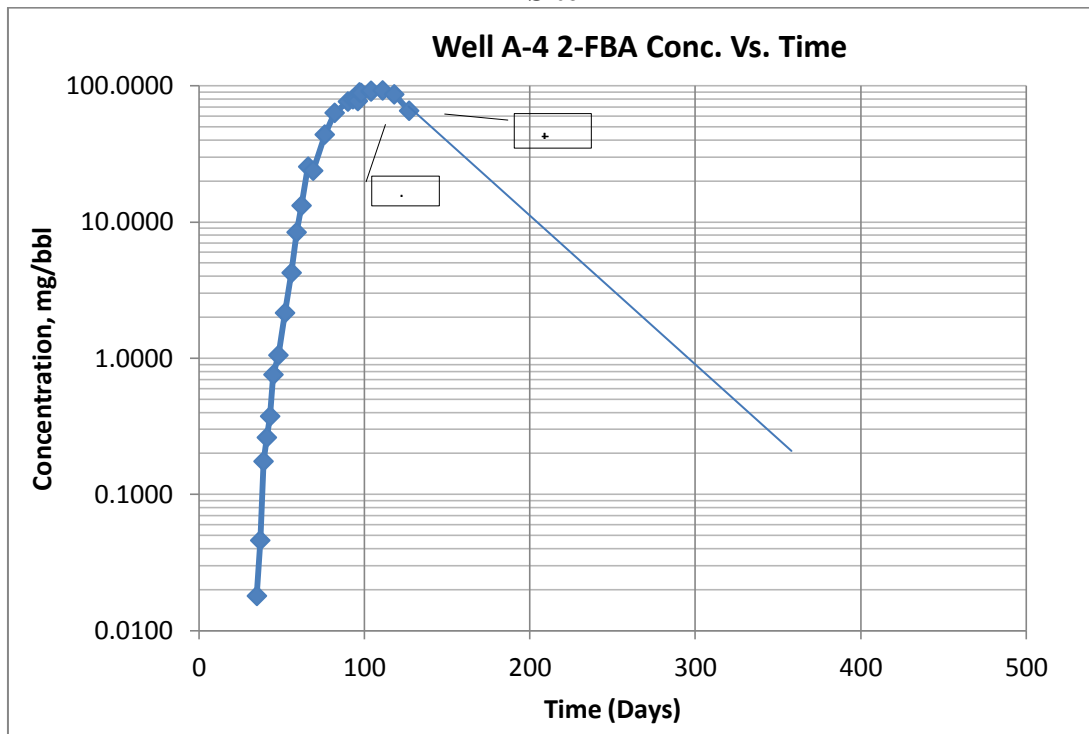


Figure 3.12. – Semi-log plot of observed 2-FBA concentration versus time for Well PA4

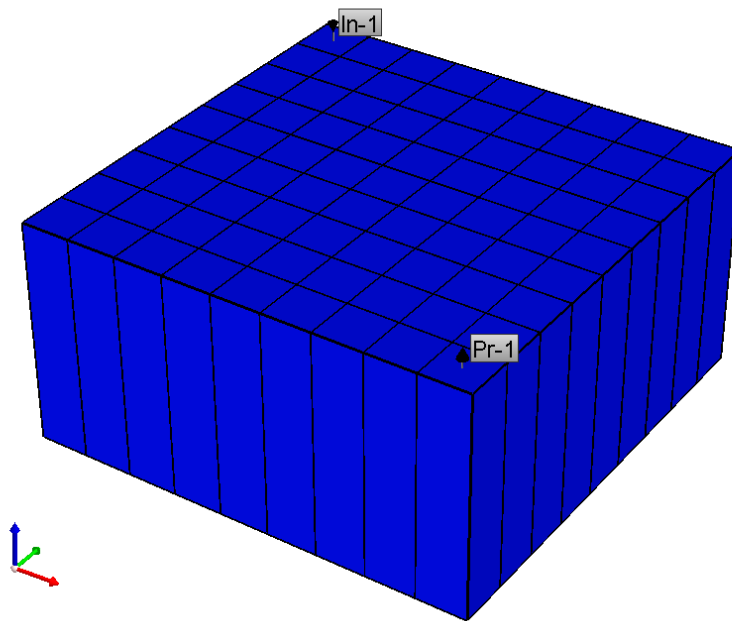


Figure 3.13. – Quadrant simulation pattern

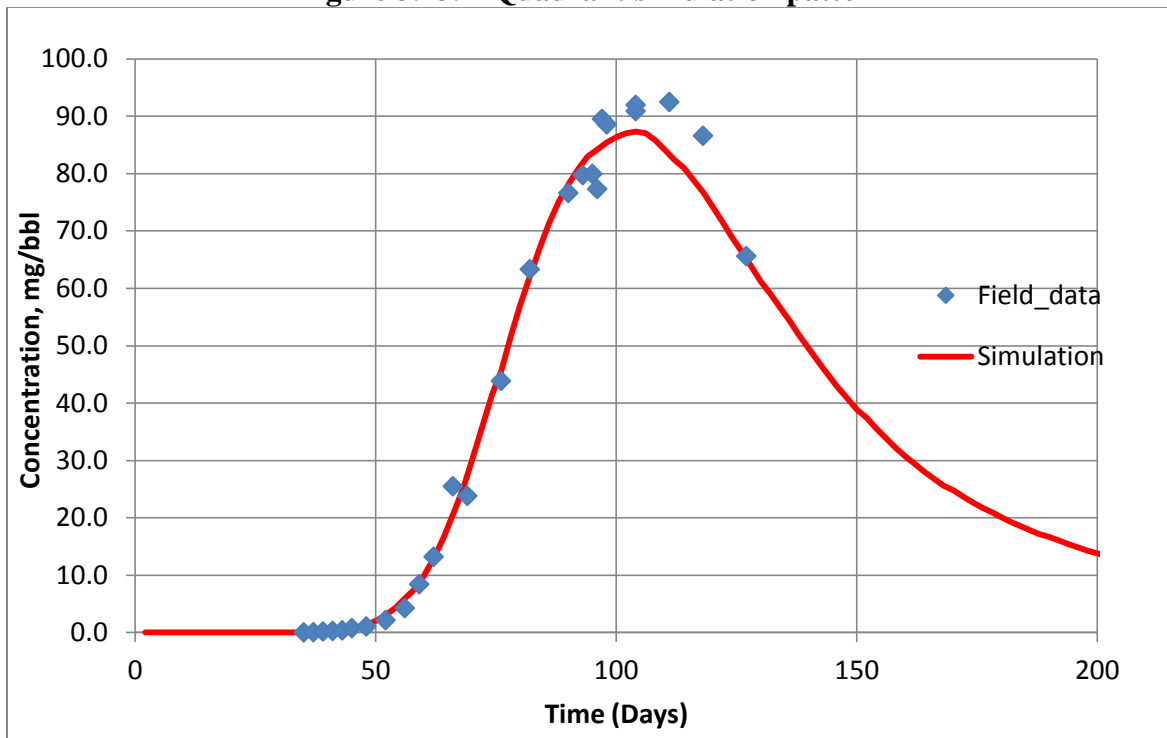


Figure 3.14. – Matched simulation results of interwell tracer test for Well PA4

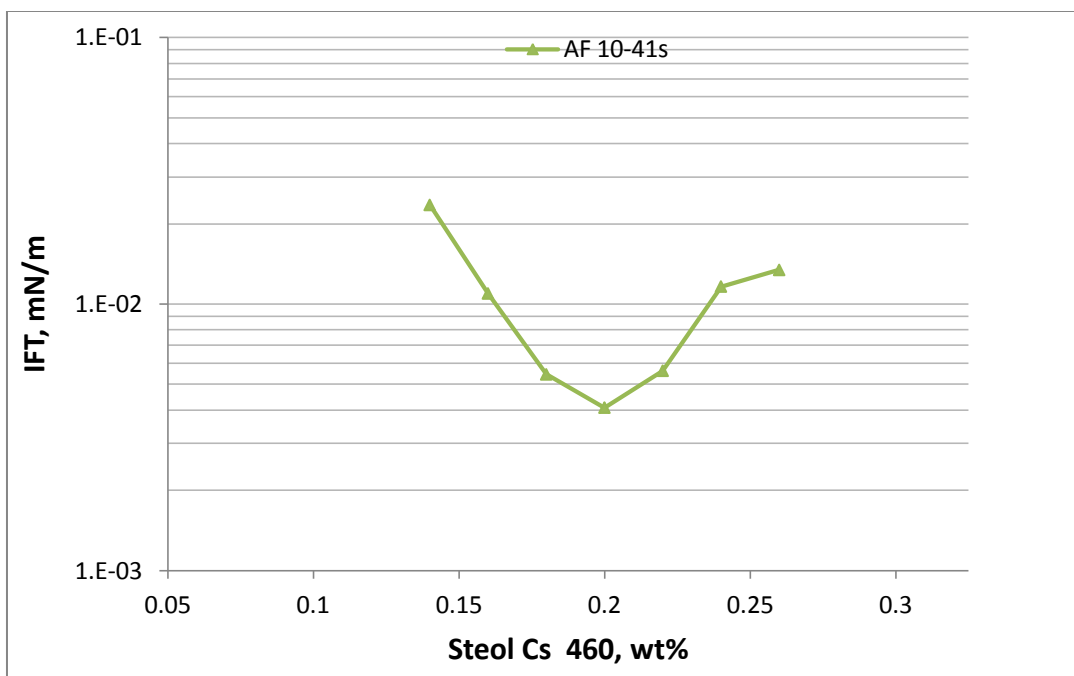


Figure 3.15. – IFT behavior of Steol CS 460 with AF-10-41s as main surfactant

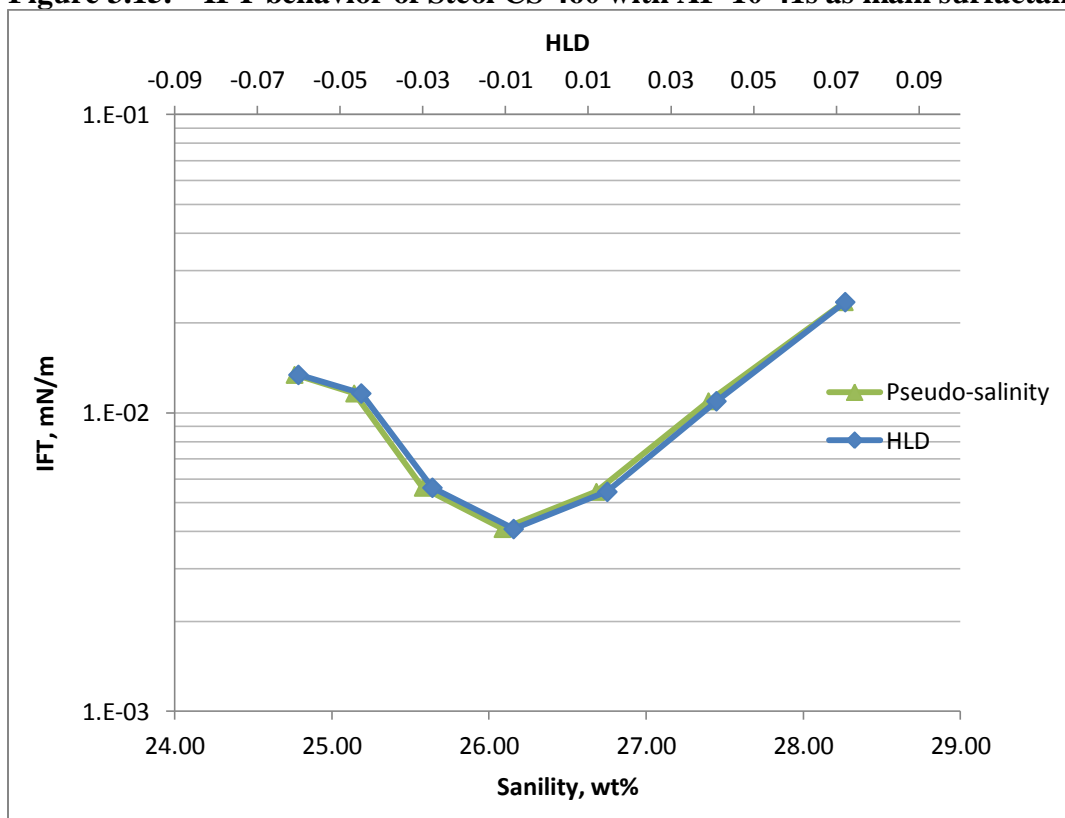


Figure 3.16. – IFT behavior of pseudo-salinity and HLD scan

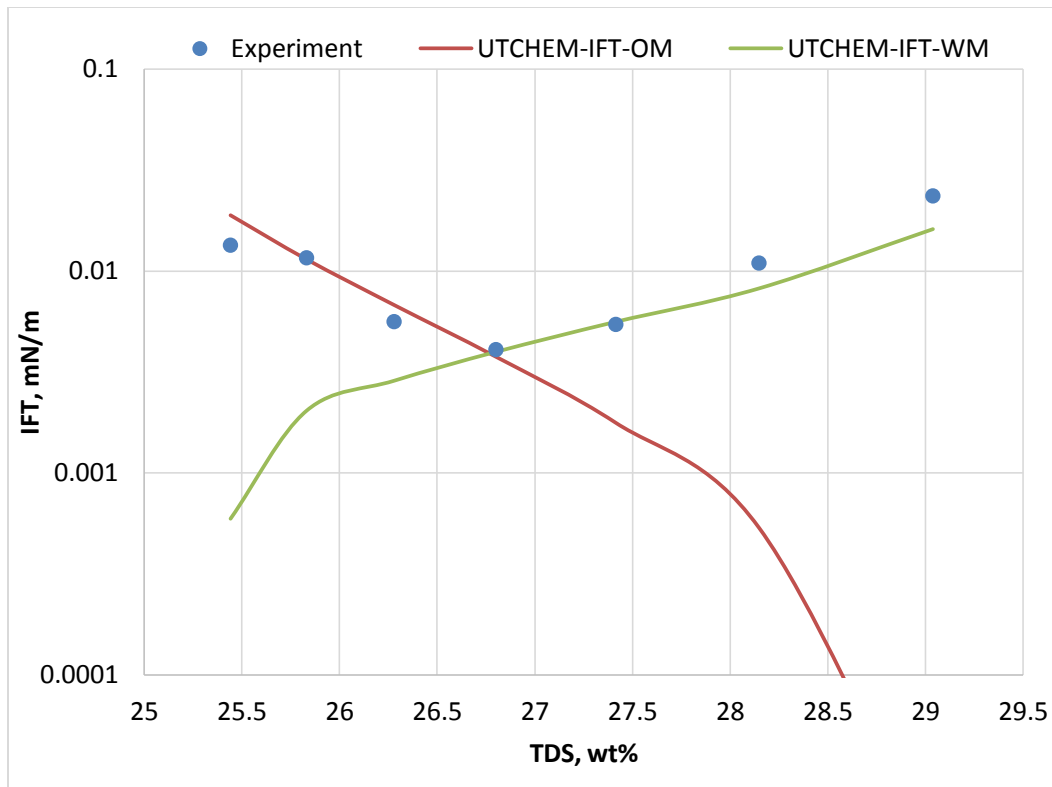


Figure 3.17. – IFT behavior matching by Hand's rule parameters

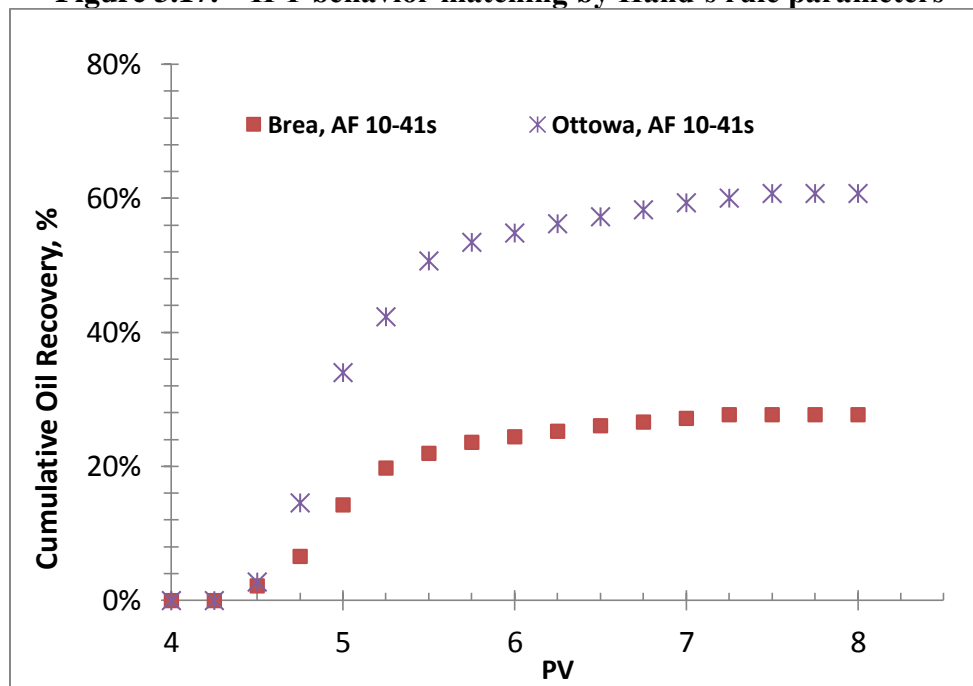


Figure 3.18. – Cumulative oil recovery of surfactant flooding

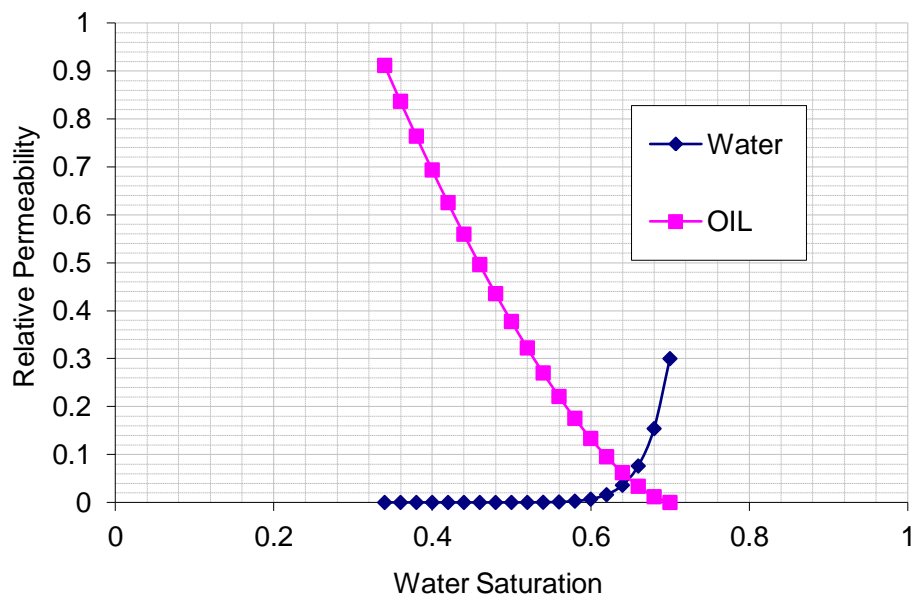


Figure 3.19. – Matched relative permeability curves for Berea sand pack flooding at low capillary number

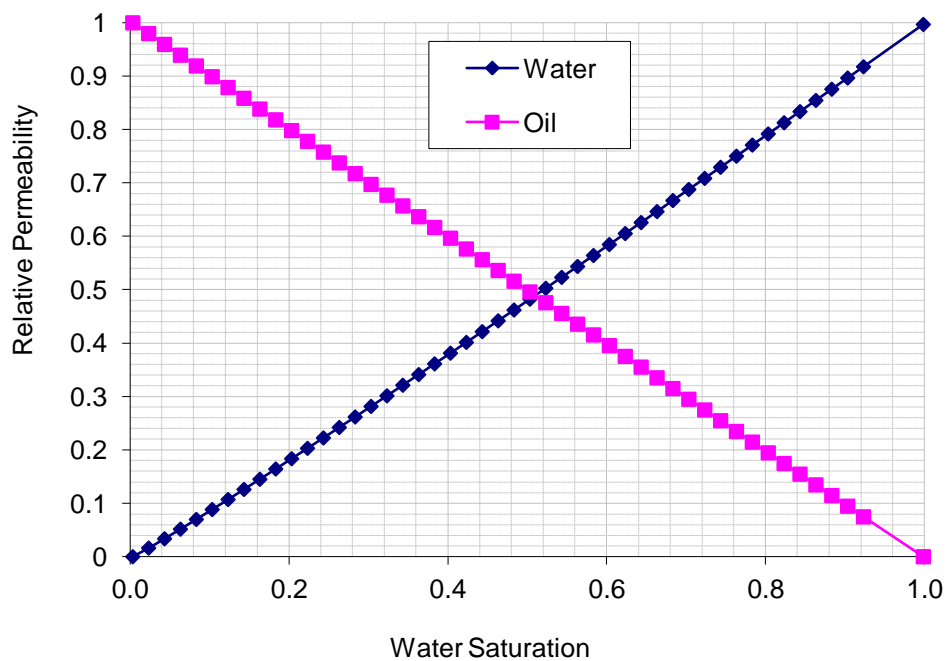


Figure 3.20. – Matched relative permeability curves for Berea sand pack flooding at high capillary number

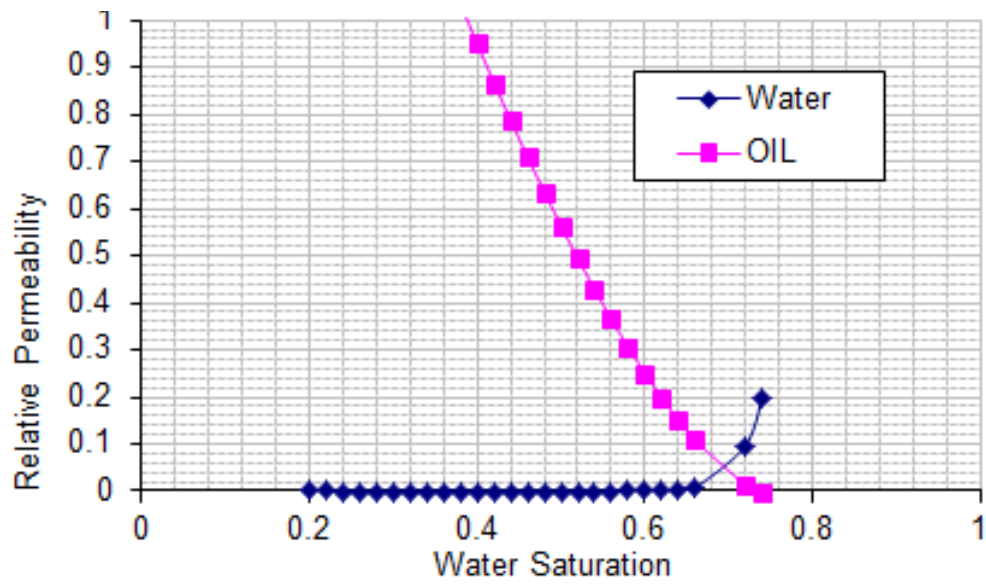


Figure 3.21. – Matched relative permeability curves for Ottawa sand pack flooding at low capillary number

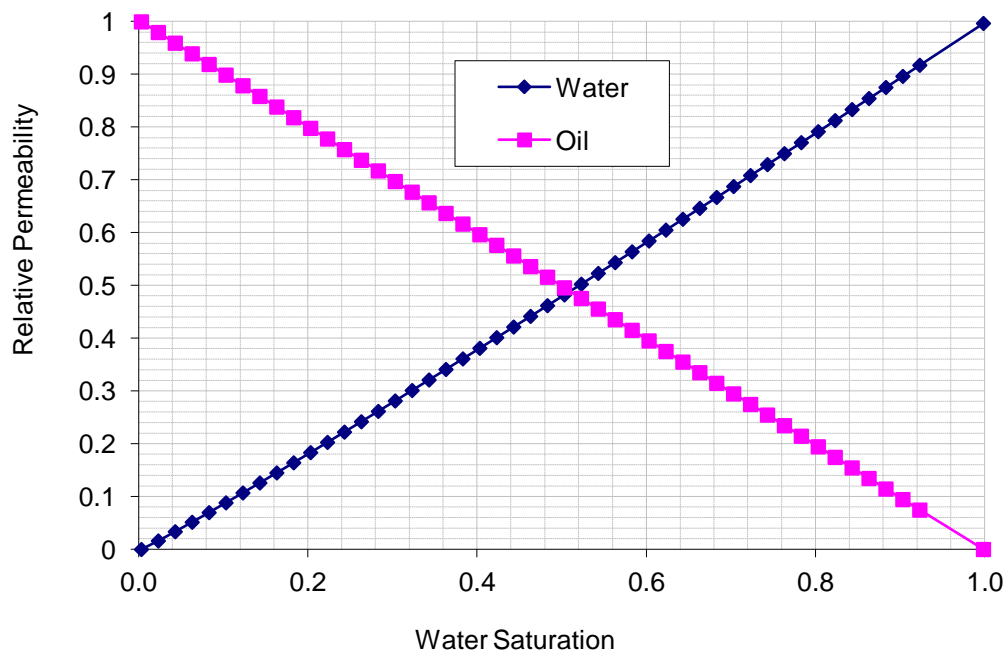


Figure 3.22. – Matched relative permeability curves for Ottawa sand pack flooding at high capillary number

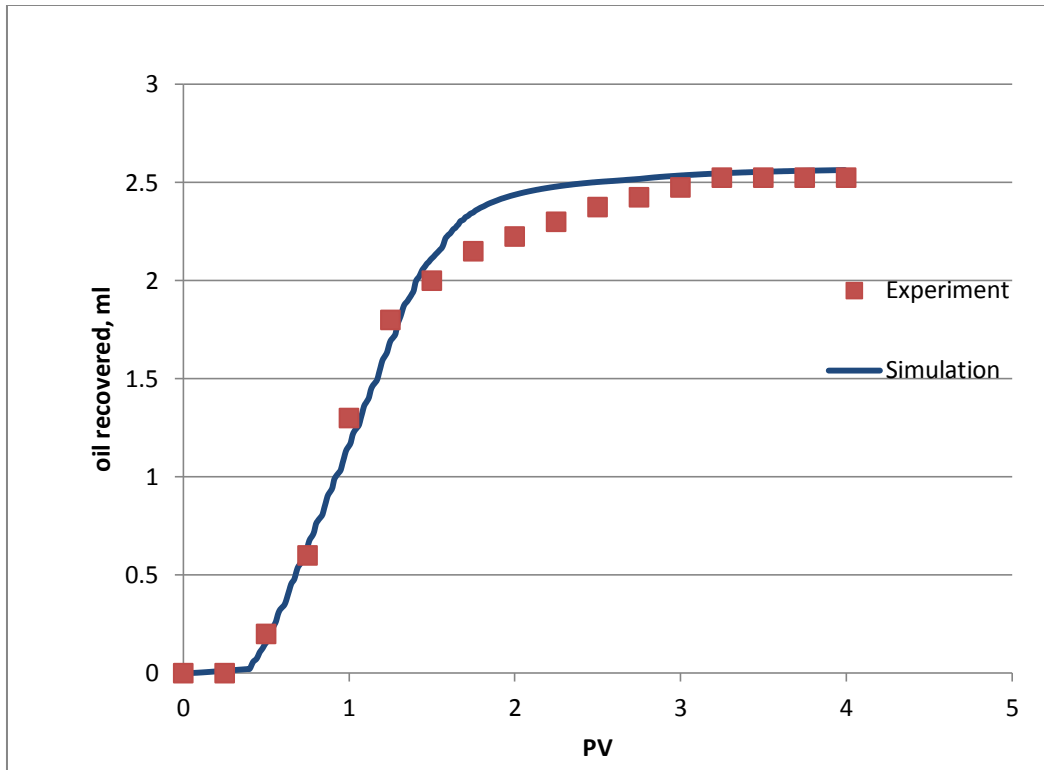


Figure 3.23. – Matched cumulative recovery of Brea sand pack surfactant flooding

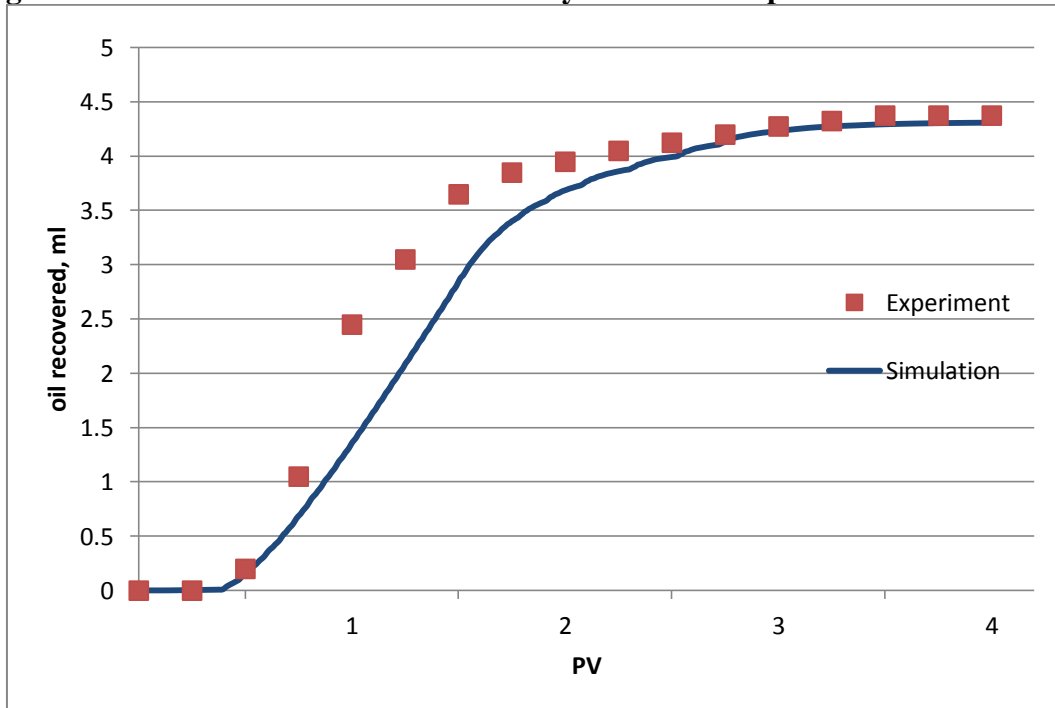


Figure 3.24. – Matched cumulative recovery of Ottawa sand pack surfactant flooding

Chapter 4. Conclusions & Recommendations

We have accomplished the key tasks as listed below in this endeavor:

1. Several potential binary and ternary surfactant-only formulations are successfully developed for high salinity formations in this study based on batch and sand-packed column experiments,
2. For tight formation, injection of polymer slug created some technical challenges to achieve high oil recovery (< 40% oil recovered in the column), thus we successfully remove polymer (s) from the surfactant formulations,
3. The newly developed surfactant-only system and formulations (between 0.5 to 0.75 total wt%) were tested in multiple single-well locations and interwell pilot test to verify their performance,
4. Pre- and post-chemical flood tracer tests were used to assess the residual saturation and the performance of oil recovery by surfactant injection,
5. Developed numerical simulation approaches and completed the effort in numerical interpretation for multiple sites and tracer tests,
 - a. Single Well Chemical Tracer Test (SWCTT) – 5 sites,
 - b. Interwell tracer test (IWTT) – 1 site,
 - c. Simulation of laboratory column test and core flood experiments – a variety of mimic reservoir conditions
6. Developed and completed geochemical study of crude oil-composition analyses, including
 - a. crude SARA fraction analysis,
 - b. fingerprints analysis,

In addition, we also completed petrophysical study of reservoir sandstones using tool such as the Nuclear Magnetic Resonance spectroscopy (NMR) method to investigate Berea sandstone.

7. On the technical transfer, we have made multiple RPSEA workshop presentations (e.g., KS, TX, CA, IN). In additional, we presented technical papers at national conferences (ACS, SPE).

We also submitted several paper abstracts to national conferences (AOCS, AIChE). We also published two journal papers and several papers are in submission stage.

The following are the significant findings of this study:

1. Applying fundamental theory (Hydrophilic-Lipophilic Difference, HLD, and concept) can significantly reduce surfactant screening time when compared to the conventional method.
2. The developed binary and ternary surfactant-only system can markedly improve recovery of common crude and viscous oil (e.g., 23 cp @ 50 °C) as confirmed in laboratory sand-pack and core flood experiments. There was exceptional correspondence between performance of the surfactant formulations between sand packs, core floods, and single well tests, which raises the issue of the necessity of performing the core floods prior to performing a single well test.
3. Results of multiple field single-well tests indicate significant trapped oil (> 90% reduction of S_{or}) can be mobilized from the target zone at various reservoir conditions and even tight formation (i.e, permeability of 15 mD).
4. Field pilot multi-wells test (Sept. 2013 – Sept., 2014) indicated that significant surfactant losses (likely due to adsorption) might interfere the field data interpretation and recovery performance. This indicates the need for development of a reliable field-scale adsorption test, as adsorption is the controlling variable in the economics of surfactant-only chemical flooding.
5. In simulation efforts, due to the complex field test processes and geological uncertainties, numerical simulation method was used to interpret the field test results. Popular reservoir simulator CMG STARS as well as UTChem were selected to model the SWCTT because

of good computational capabilities and chemical reaction features. The HLD method was adopted to modify UTChem for surfactant-only flooding without use of a salinity gradient.

6. Based on the resulting matching profiles of pre-SWCTT and post-SWCTT Sor at multiple reservoirs and locations, we successfully exhibited good surfactant flooding efficiency under various reservoir locations.
7. Based on fingering effort, we observed that crude oil fractions could have impact on the interfacial tensions (IFTs), which is the most critical parameter of EOR.
8. Asphaltenes from different crude oils contain various components, which indicate these crudes may come from different original materials and reservoir conditions.

Recommendations of future work:

1. Field pilot multi-wells test: additional sites would be selected and screened for potential surfactant flooding. And more pilot tests are anticipated in next twelve to twenty four months (2016-17) based on the encouraging results of multiple single-well tests and some challenging tasks we met and lessons learned from the first field pilot interwell test.
2. Streamline the design protocols for field pilot test based on the conclusions of this RPSEA effort. Use of the HLD equation and concept greatly reduces formulation efforts and sand pack performance is an excellent surrogate for performance in the single well test; in general oil mobilization in the single well test exceeded that in the sand pack tests.

3. Modify the single well test to measure surfactant retention by the reservoir rock.

Surfactant adsorption should now be considered the most important remaining barrier to commercialization of surfactant-only cEOR.

4. Examine various approaches to reduction of surfactant adsorption, beyond possible modification of the structure of the surfactant. The use of sacrificial agents, including polyelectrolytes and nanocarriers should be a focus of future surfactant-only chemical flooding EOR research.

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